Supporting Information

Oxidative Heck Reaction of Glycals and Aryl Hydrazines: A Palladium-Catalyzed *C*-Glycosylation

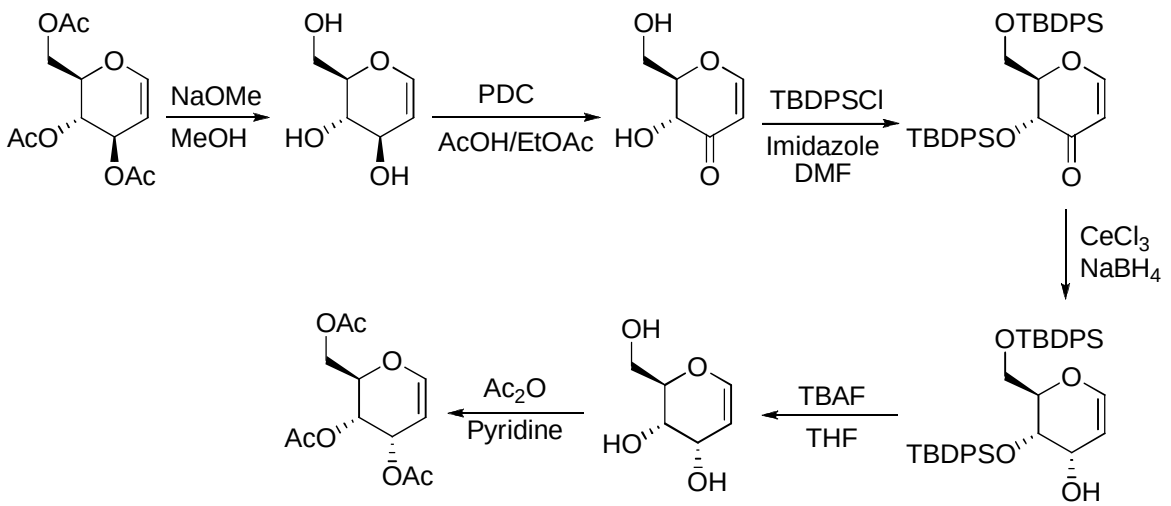
Yaguang Bai, Le Mai Hoang Kim, Hongze Liao and Xue-Wei Liu*

Division of Chemistry and Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371 Singapore

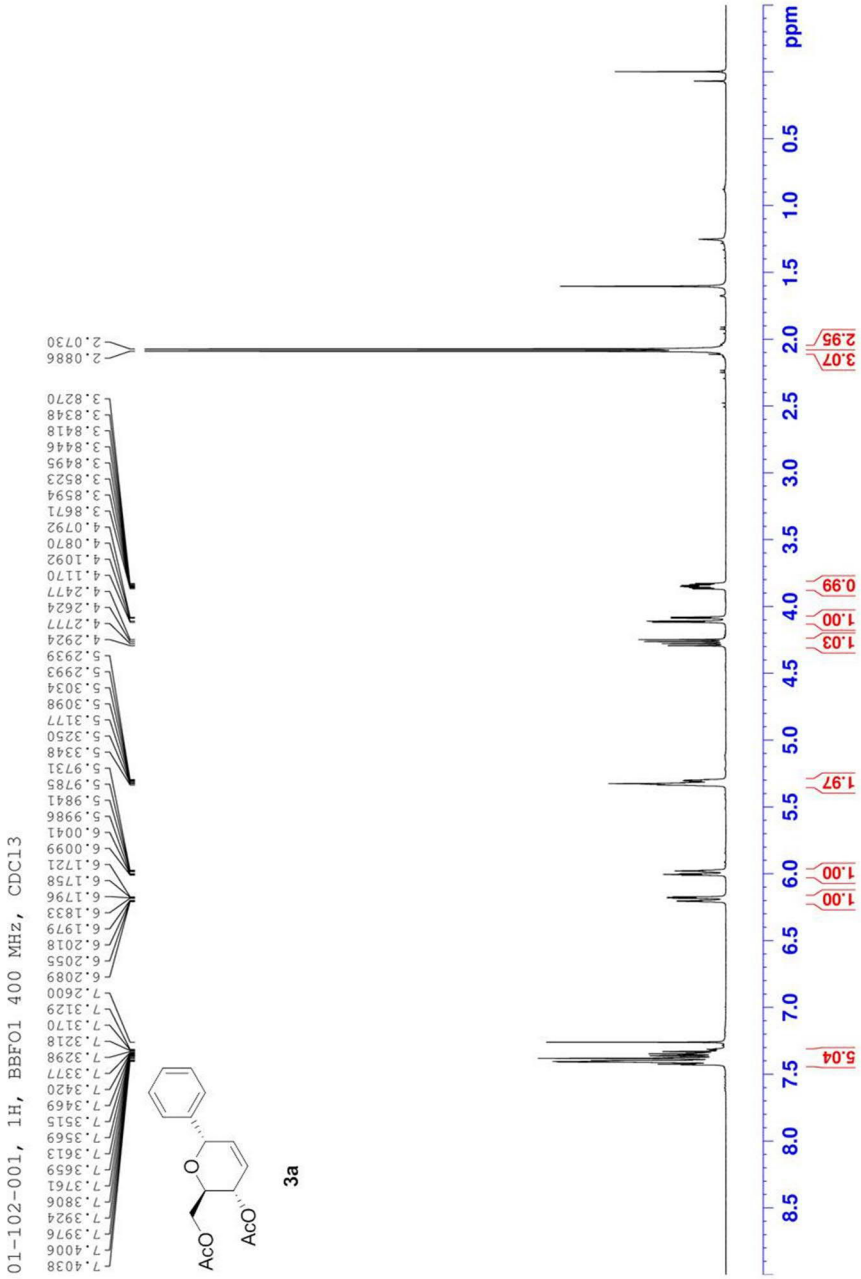
Table of Contents:

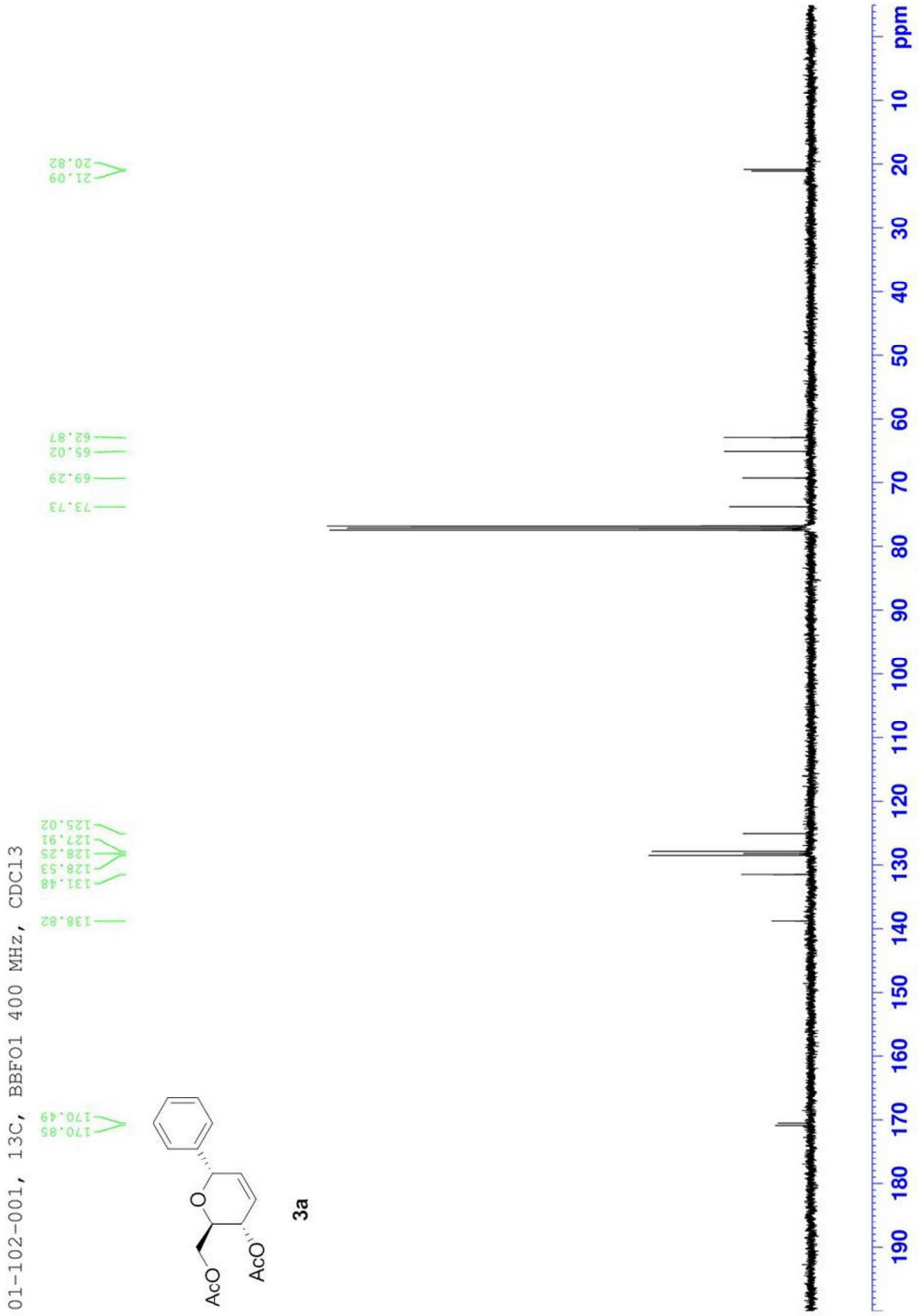
General: All the reactions were carried out in a flame or oven dried glassware with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Organic solutions were concentrated under reduced pressure by rotary evaporation with a water bath (temperature below 40 °C). Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates using UV light at 254 nm as a visualizing agent and a $KMnO_4$ solution as stain. Product purification by flash column chromatography was accomplished using silica gel 60 (0.010–0.063 nm). Technical grade solvents were used for chromatography and were distilled prior to use. Optical rotations were measured in $CHCl_3$ with a 1 cm cell (*c* given in g/100 mL). NMR spectra were recorded at room temperature on 400 MHz. The residual solvent signals were taken as the reference (7.26 ppm for 1H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$). Sometimes the TMS signal at 0.0 ppm was used an internal standard for ^{1}H NMR spectra. Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal. HR-MS (ESI) spectra were recorded on a Q-Tof mass spectrometer.

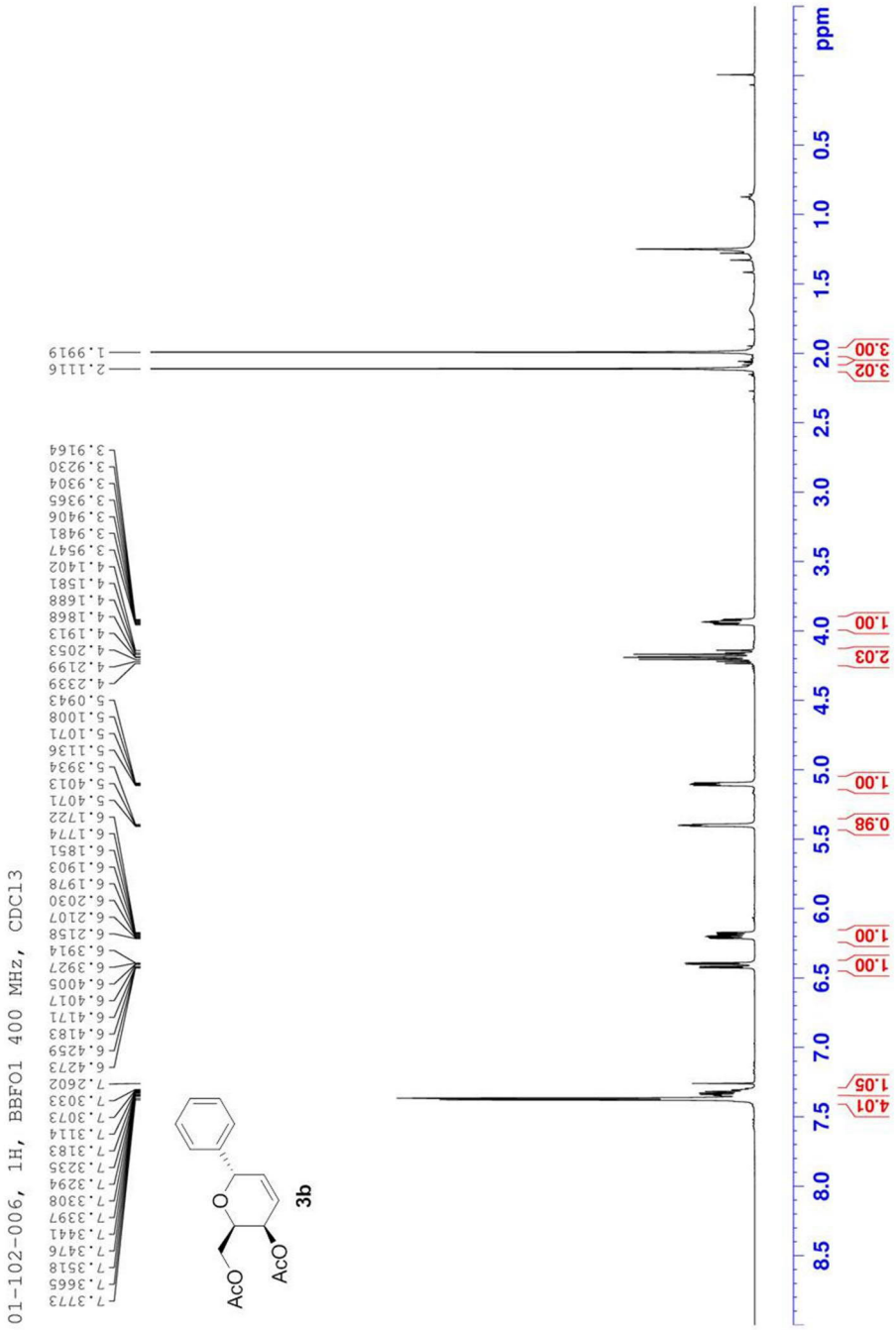
Synthesis of 3-inverted acetyl glucal ((2R,3S,4S)-2-(acetoxymethyl)-3,4-dihydro-2H-pyran-3,4-diyl diacetate) from commercially available acetyl glucal ((2R,3S,4R)-2-(acetoxymethyl)-3,4-dihydro-2H-pyran-3,4-diyl diacetate)

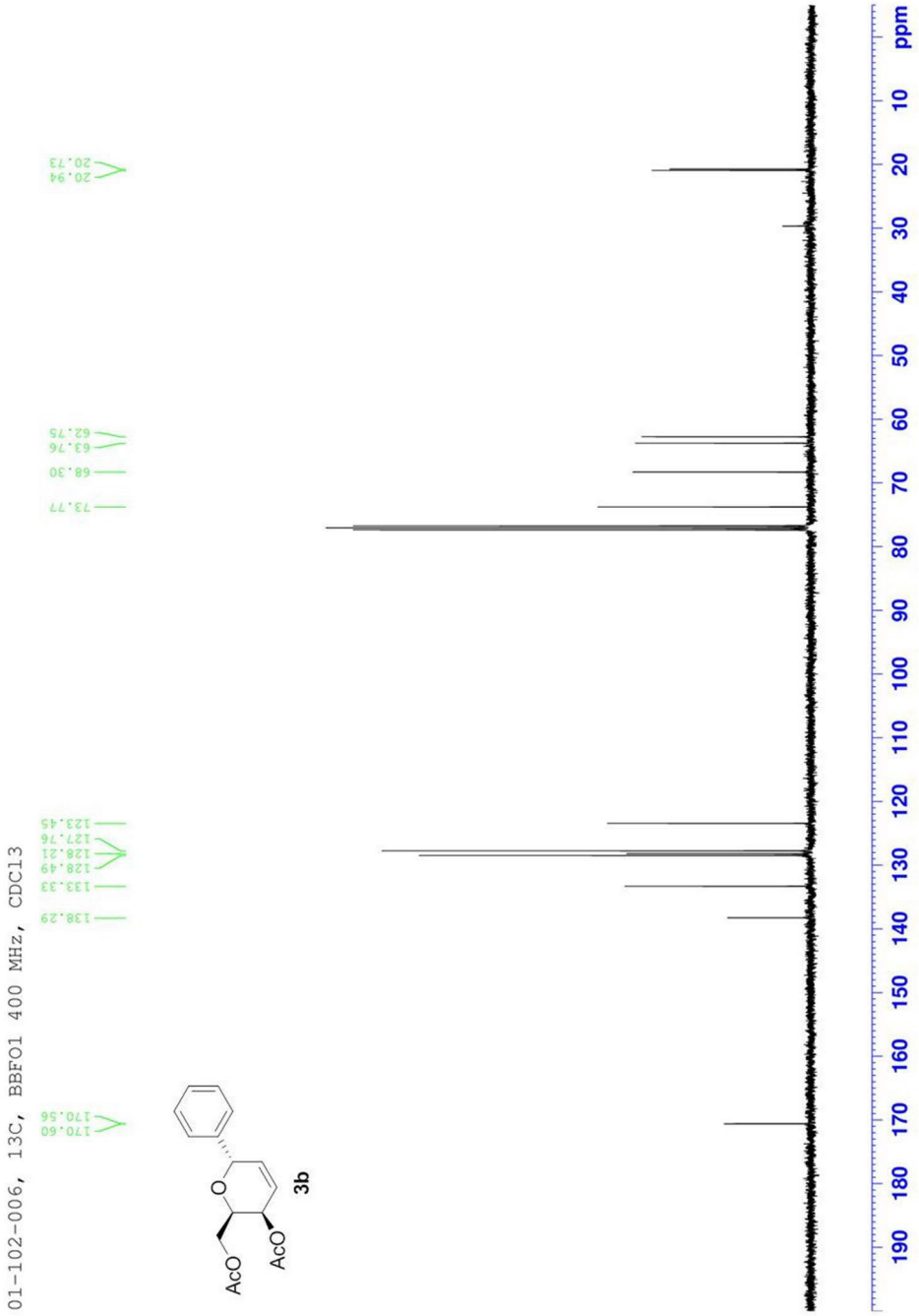


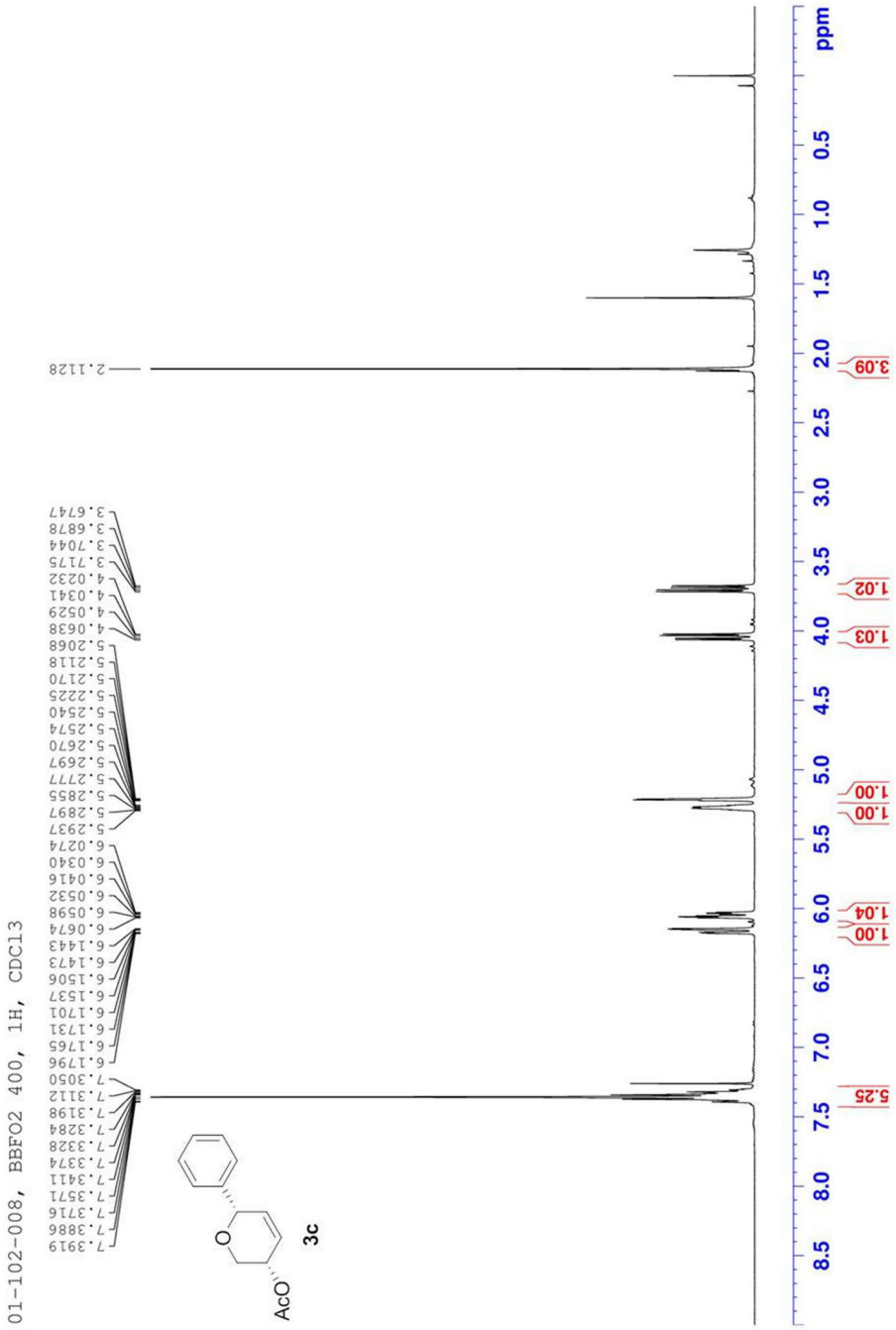
Copies of ^{1}H and ^{13}C NMR spectrum

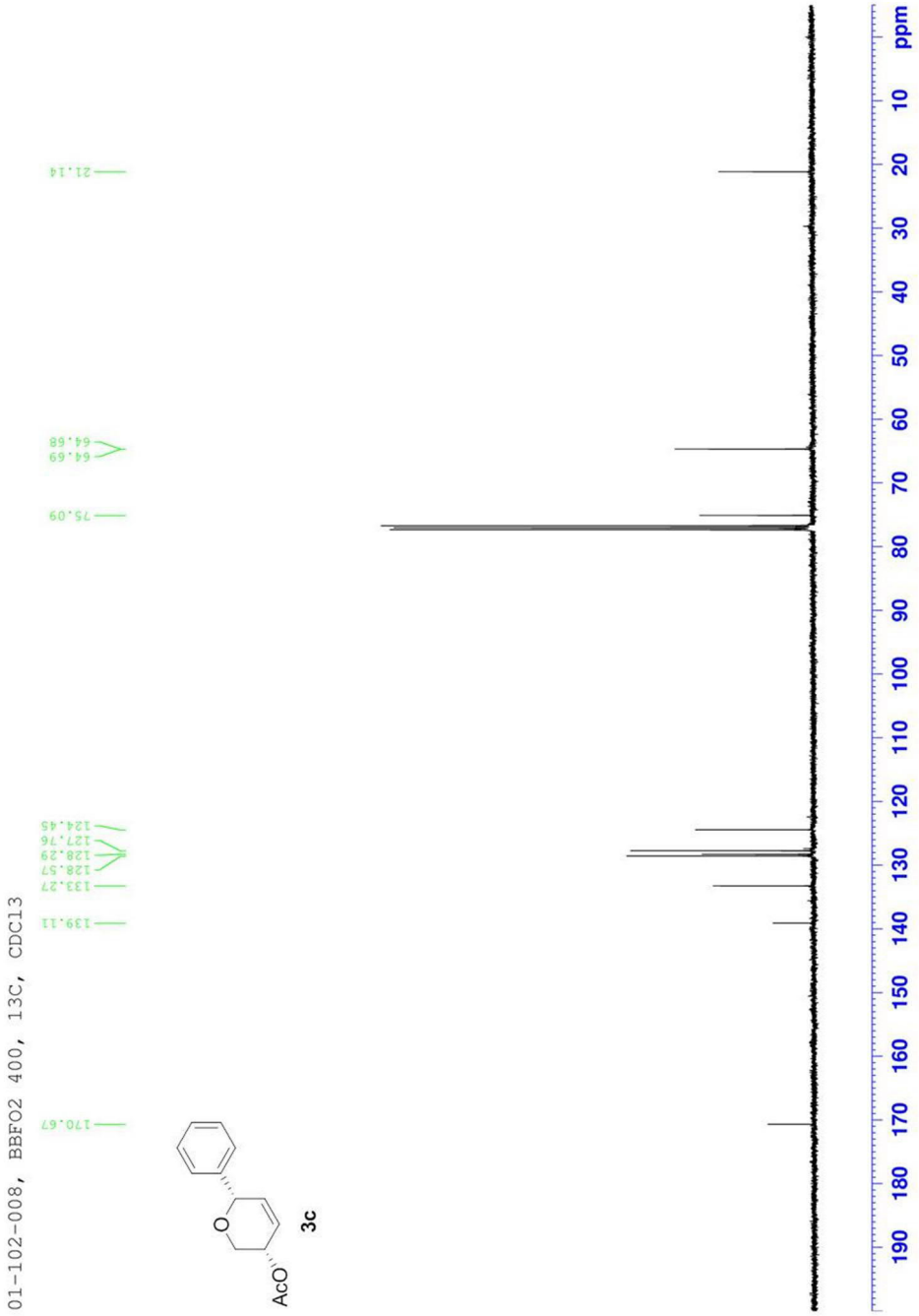


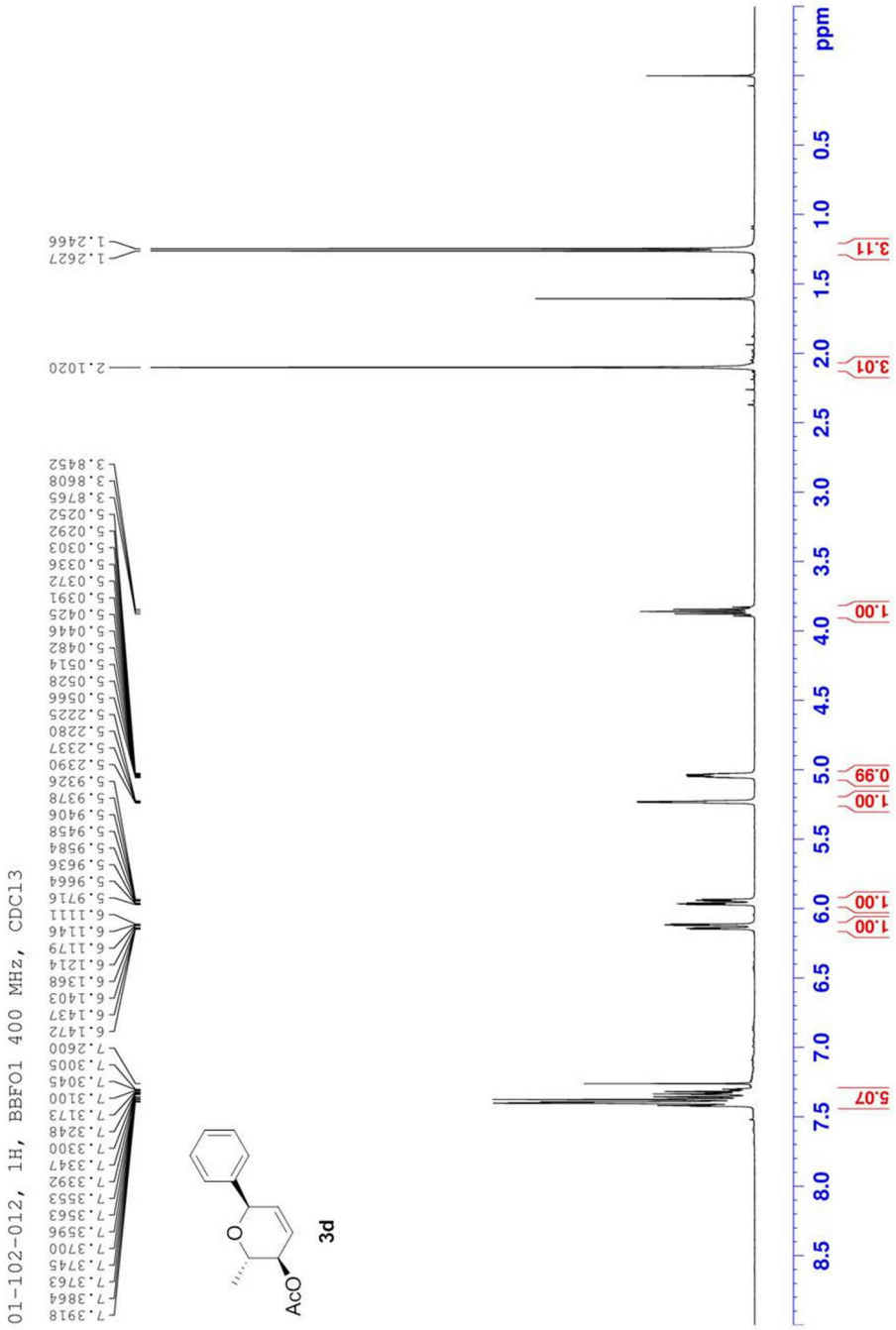

01-102-001, 13C, BBFO1 400 MHz, CDCl3
170.85
170.49
138.82
131.48
128.53
128.25
127.91
125.02
73.73
69.29
65.02
62.87
21.09
20.82
AcO
AcO
O
3a
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

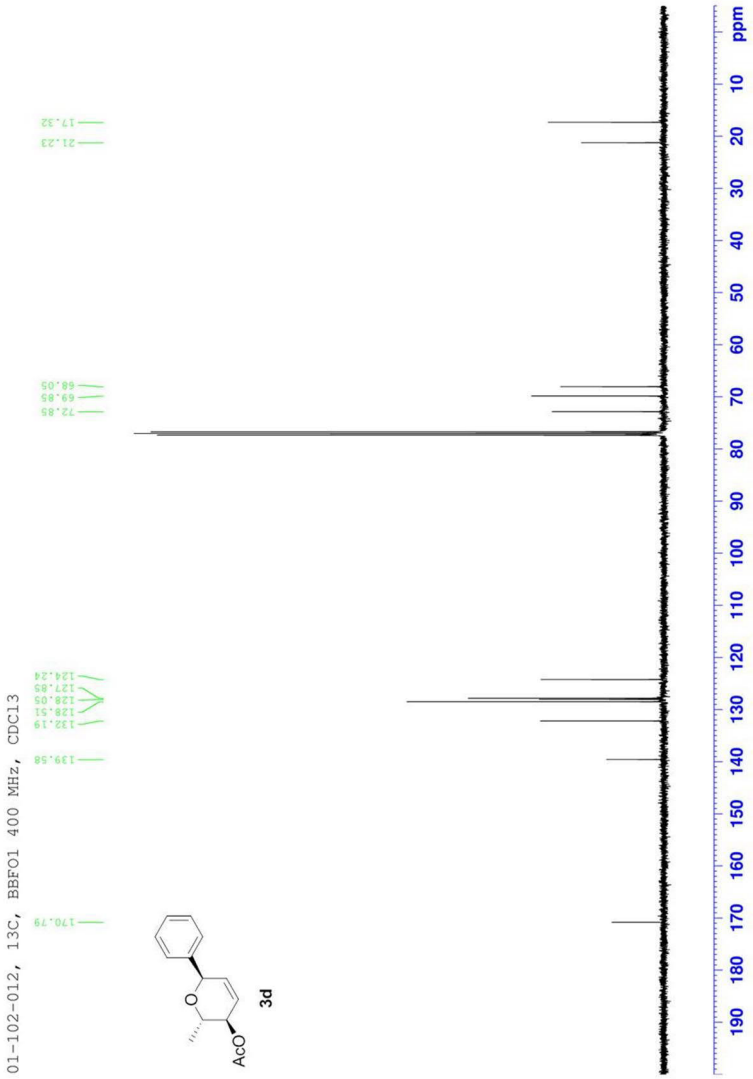

01-102-006, 1H, BBFO1 400 MHz, CDCl3
7.3773
7.3665
7.3518
7.3476
7.3441
7.3397
7.3308
7.3294
7.3235
7.3183
7.3114
7.3073
7.3033
7.2602
6.4273
6.4259
6.4183
6.4171
6.4017
6.4005
6.3927
6.3914
6.2158
6.2107
6.2030
6.1978
6.1903
6.1851
6.1774
6.1722
5.4071
5.4013
5.3934
5.1136
5.1071
5.1008
5.0943
4.2339
4.2199
4.2053
4.1913
4.1868
4.1688
4.1581
4.1402
3.9547
3.9481
3.9406
3.9365
3.9304
3.9230
3.9164
2.1116
1.9919
AcO
AcO
O
3b
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
4.01
1.05
1.00
1.00
1.00
0.98
1.00
2.03
1.00
3.02
3.00

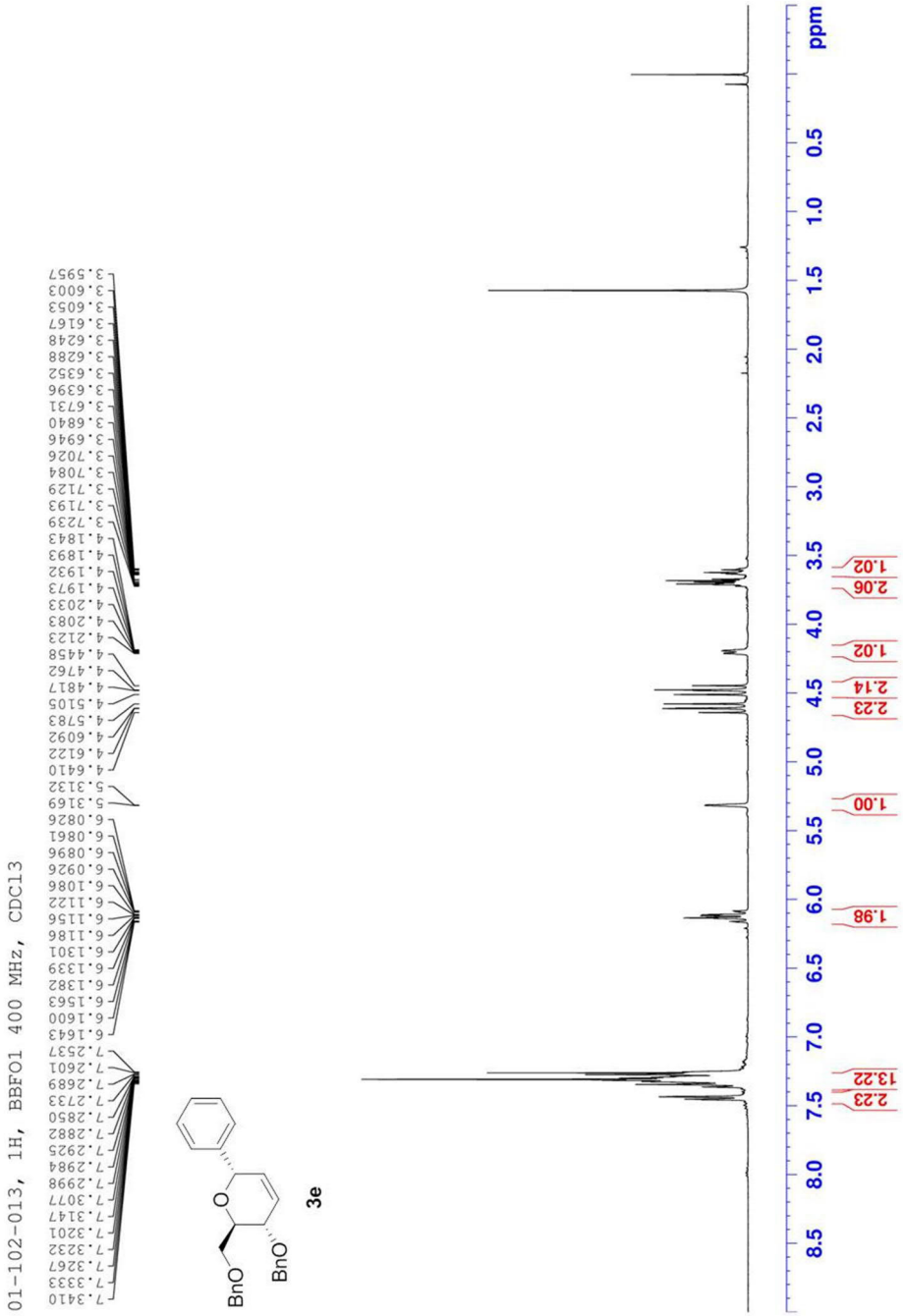

01-102-006, 13C, BBFO1 400 MHz, CDCl3
170.60
170.56
138.29
133.33
128.49
128.21
127.76
123.45
73.77
68.30
63.76
62.75
20.94
20.73
AcO
AcO
O
3b
ppm

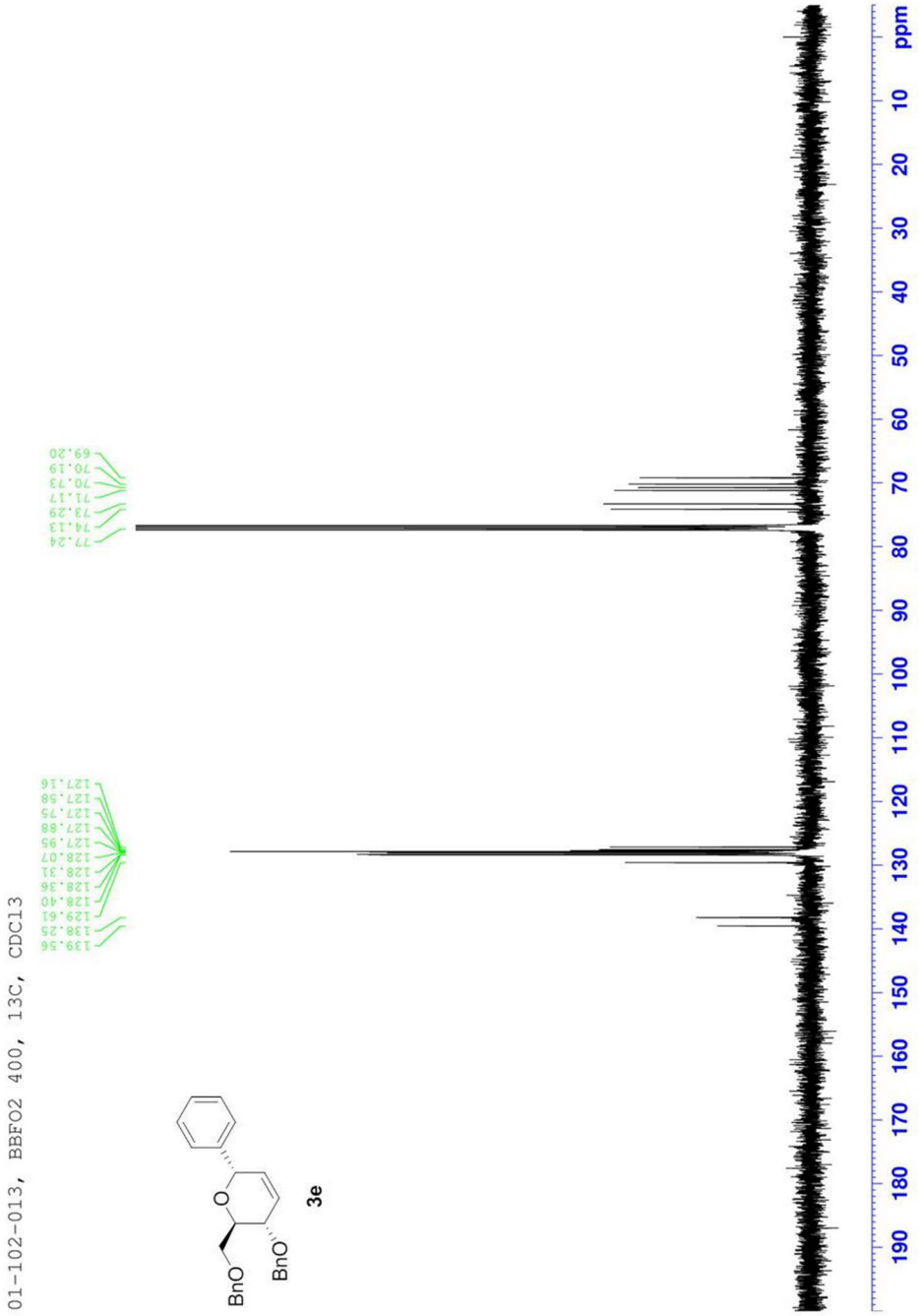

01-102-008, BBFO2 400, 1H, CDCl3
7.3919
7.3886
7.3716
7.3571
7.3411
7.3374
7.3328
7.3284
7.3198
7.3112
7.3050
6.1796
6.1765
6.1731
6.1701
6.1537
6.1506
6.1473
6.1443
6.0674
6.0598
6.0532
6.0416
6.0340
6.0274
5.2937
5.2897
5.2855
5.2777
5.2697
5.2670
5.2574
5.2540
5.2225
5.2170
5.2118
5.2068
4.0638
4.0529
4.0341
4.0232
3.7175
3.7044
3.6878
3.6747
2.1128
AcO
O
3c
5.25
1.00
1.04
1.00
1.00
1.00
1.03
1.02
3.09
ppm

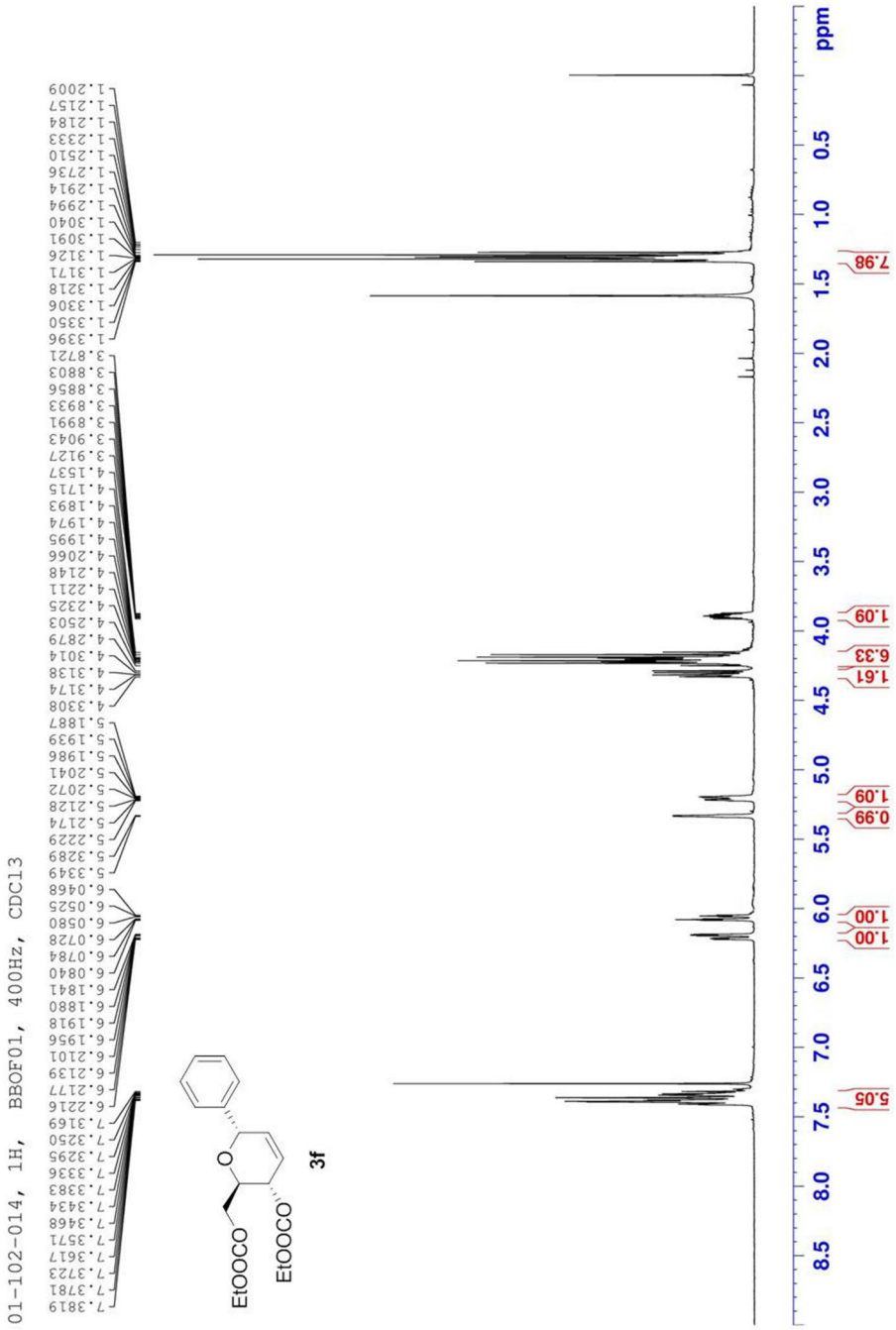

01-102-008, BBFO2 400, 13C, CDC13
170.67
139.11
133.27
128.57
128.29
127.76
124.45
75.09
64.69
64.68
21.14
AcO
O
3c
ppm

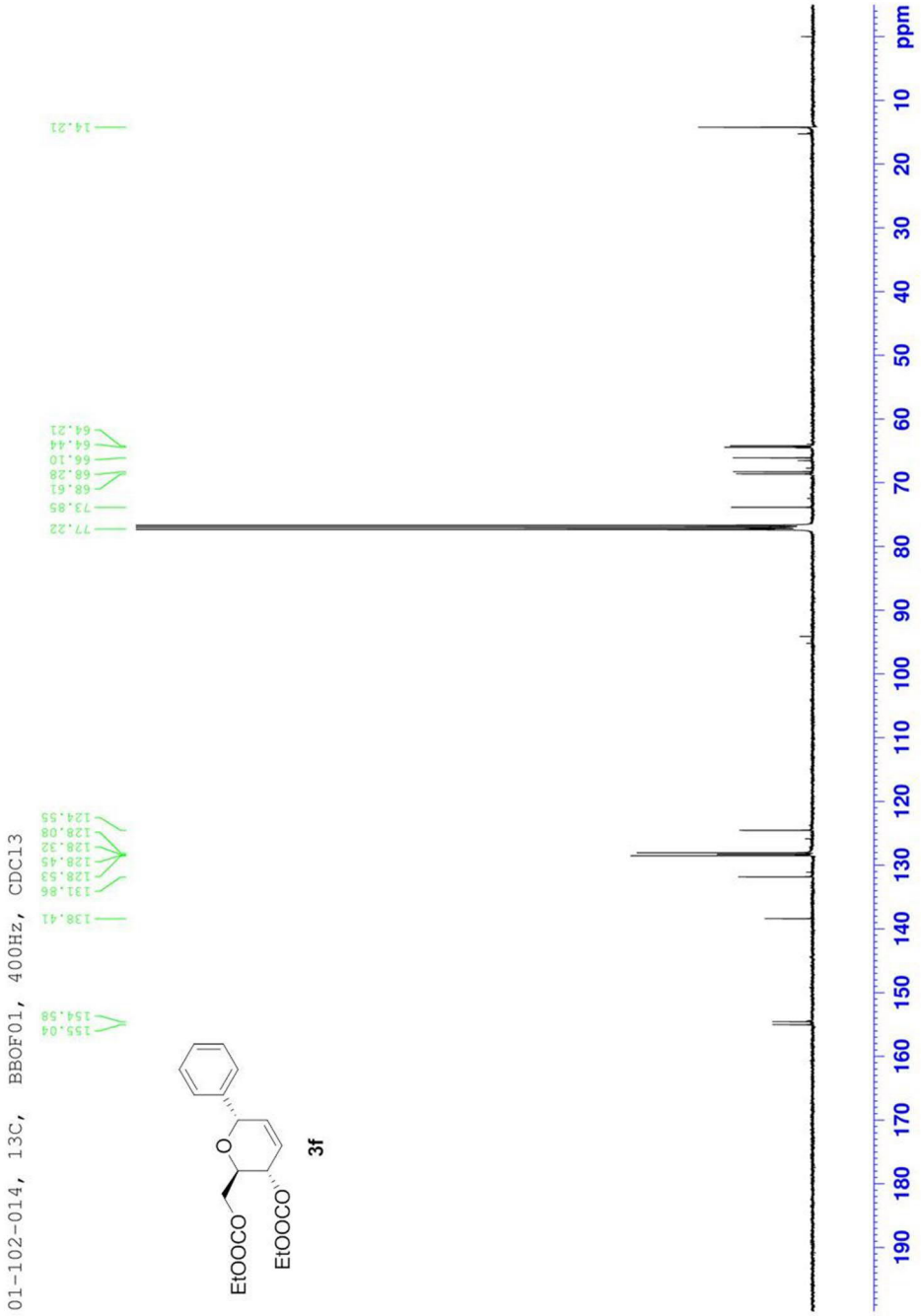

01-102-012, 1H, BBFO1 400 MHz, CDCl3
7.3918
7.3864
7.3763
7.3745
7.3700
7.3596
7.3563
7.3553
7.3392
7.3347
7.3300
7.3248
7.3173
7.3100
7.3045
7.3005
7.2600
6.1472
6.1437
6.1403
6.1368
6.1214
6.1179
6.1146
6.1111
5.9716
5.9664
5.9636
5.9584
5.9458
5.9406
5.9378
5.9326
5.2390
5.2337
5.2280
5.2225
5.0566
5.0528
5.0514
5.0482
5.0446
5.0425
5.0391
5.0372
5.0336
5.0303
5.0292
5.0252
3.8765
3.8608
3.8452
2.1020
1.2627
1.2466
AcO
O
3d
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
5.07
1.00
1.00
1.00
1.00
0.99
1.00
3.01
3.11

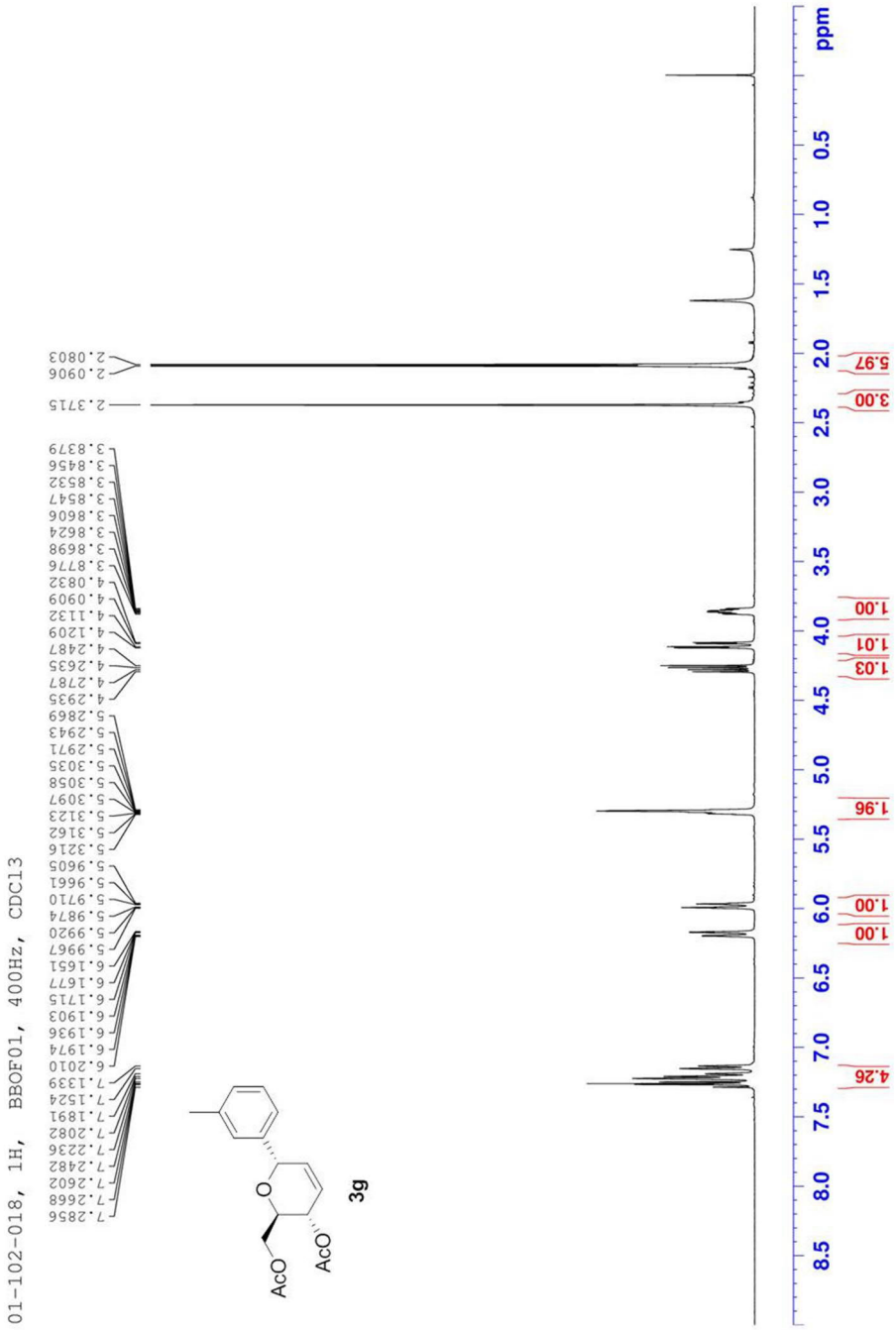

01-102-012, 13C, BBFO1 400 MHz, CDCl3
170.79
139.58
132.19
128.51
128.05
127.85
124.24
72.85
69.85
68.05
21.23
17.32
AcO
O
3d
ppm

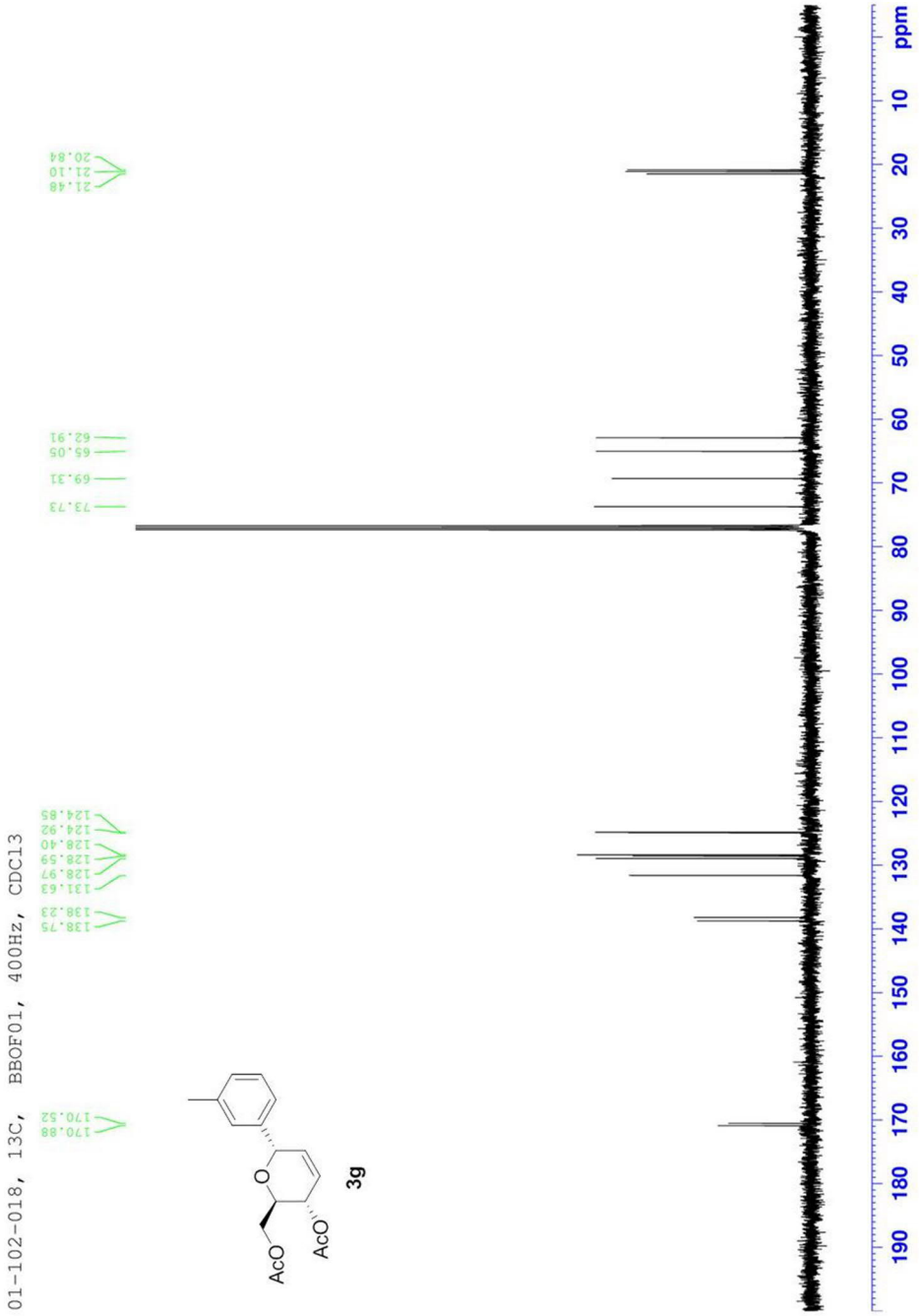

01-102-013, 1H, BBFO1 400 MHz, CDCl3
7.3410
7.3333
7.3267
7.3232
7.3201
7.3147
7.3077
7.2998
7.2984
7.2925
7.2882
7.2850
7.2733
7.2689
7.2601
7.2537
6.1643
6.1600
6.1563
6.1382
6.1339
6.1301
6.1186
6.1156
6.1122
6.1086
6.0926
6.0896
6.0861
6.0826
5.3169
5.3132
4.6410
4.6122
4.6092
4.5783
4.5105
4.4817
4.4762
4.4458
4.2123
4.2083
4.2033
4.1973
4.1932
4.1893
4.1843
3.7239
3.7193
3.7129
3.7084
3.7026
3.6946
3.6840
3.6731
3.6396
3.6352
3.6288
3.6248
3.6167
3.6053
3.6003
3.5957
BnO
O
BnO
3e
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.23
13.22
1.98
1.00
2.23
2.14
1.02
2.06
1.02

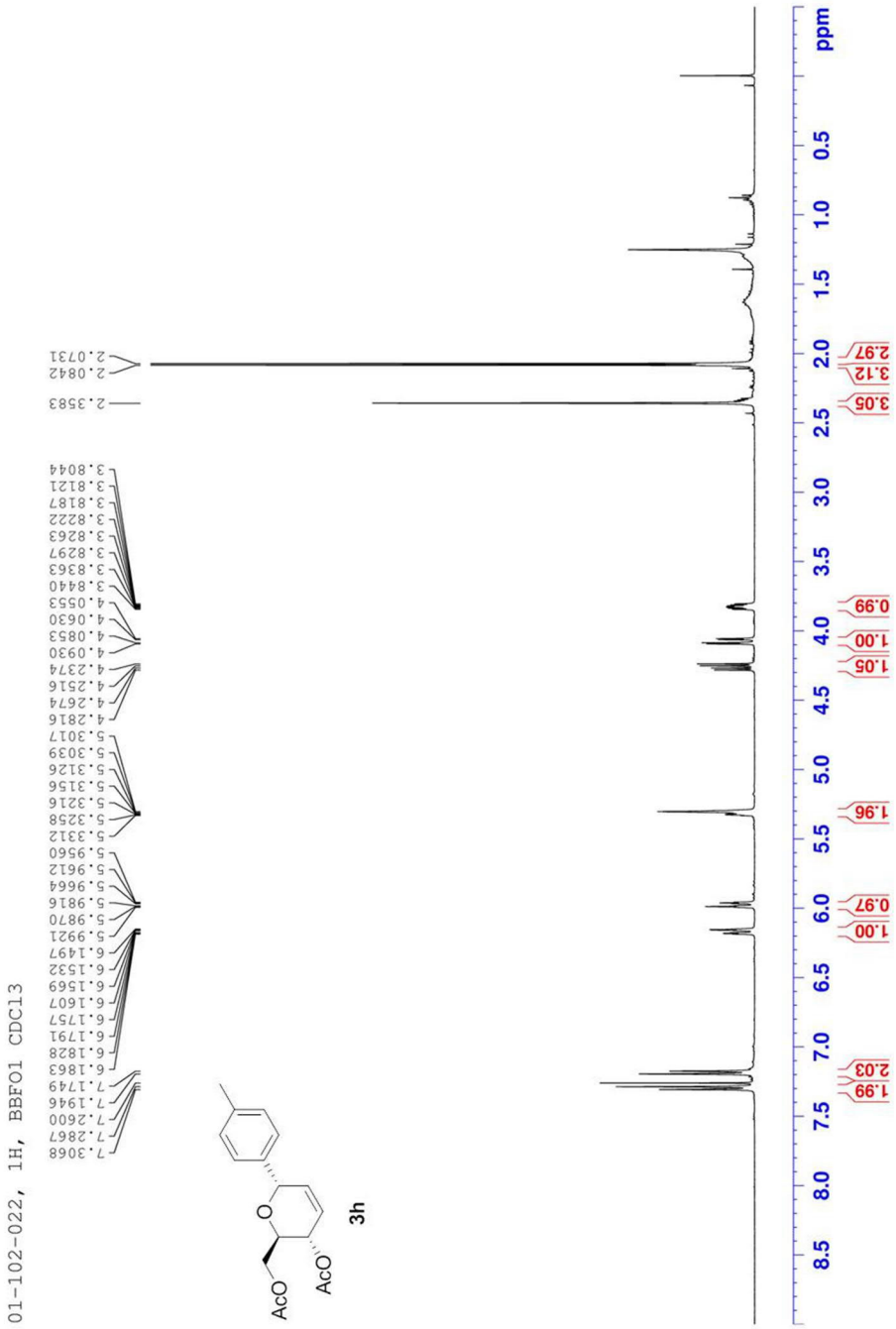

01-102-013, BBFO2 400, 13C, CDCl3
139.56
138.25
129.61
128.40
128.36
128.31
128.07
127.95
127.88
127.75
127.58
127.16
77.24
74.13
73.29
71.17
70.73
70.19
69.20
BnO
BnO
O
3e
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

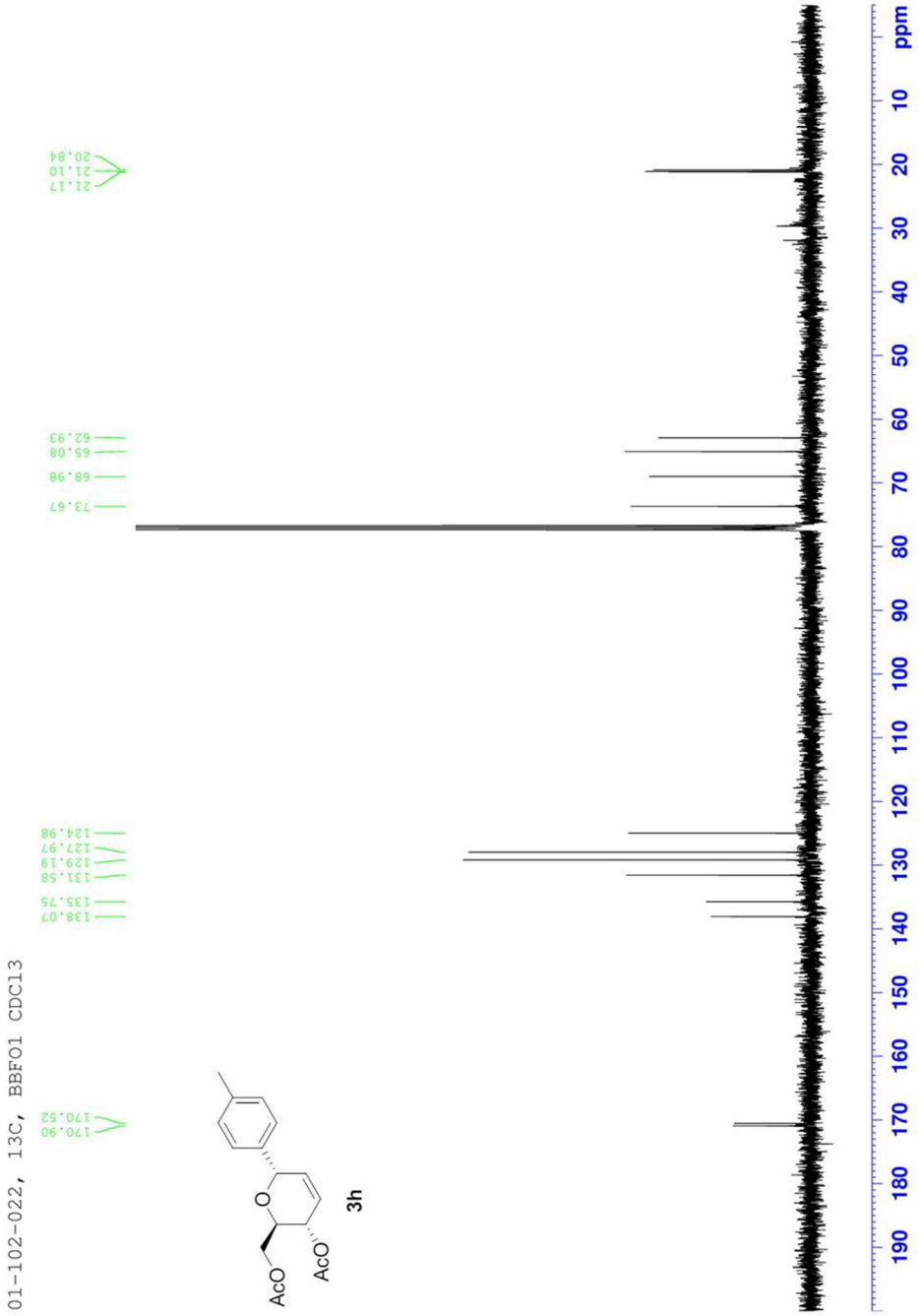

01-102-014, 1H, BBOF01, 400Hz, CDCl3
7.3819
7.3781
7.3723
7.3617
7.3571
7.3468
7.3434
7.3383
7.3336
7.3295
7.3250
7.3169
6.2216
6.2177
6.2139
6.2101
6.1956
6.1918
6.1880
6.1841
6.0840
6.0784
6.0728
6.0580
6.0525
6.0468
5.3349
5.3289
5.2229
5.2174
5.2128
5.2072
5.2041
5.1986
5.1939
5.1887
4.3308
4.3174
4.3138
4.3014
4.2879
4.2503
4.2325
4.2211
4.2148
4.2066
4.1995
4.1974
4.1893
4.1715
4.1537
3.9127
3.9043
3.8991
3.8933
3.8856
3.8803
3.8721
1.3396
1.3350
1.3306
1.3218
1.3171
1.3126
1.3091
1.3040
1.2994
1.2914
1.2736
1.2510
1.2333
1.2184
1.2157
1.2009
EtOOCO
EtOOCO
O
3f
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
7.98
1.09
6.33
1.61
1.09
0.99
1.00
1.00
5.05

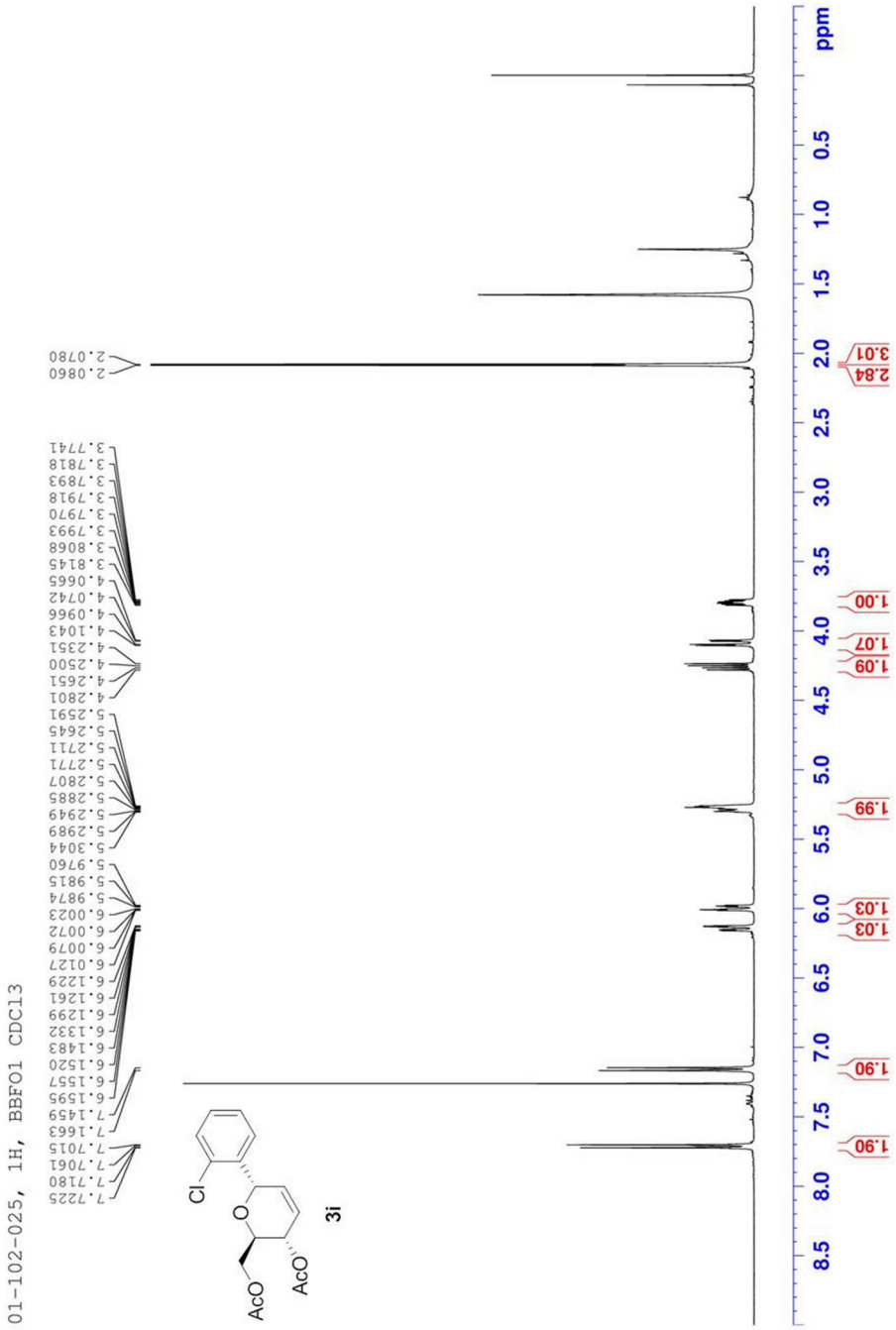

01-102-014, 13C, BBOF01, 400Hz, CDCl3
155.04
154.58
138.41
131.86
128.53
128.45
128.32
128.08
124.55
77.22
73.85
68.61
68.28
66.10
64.44
64.21
14.21
EtOOCO
EtOOCO
O
3f
ppm

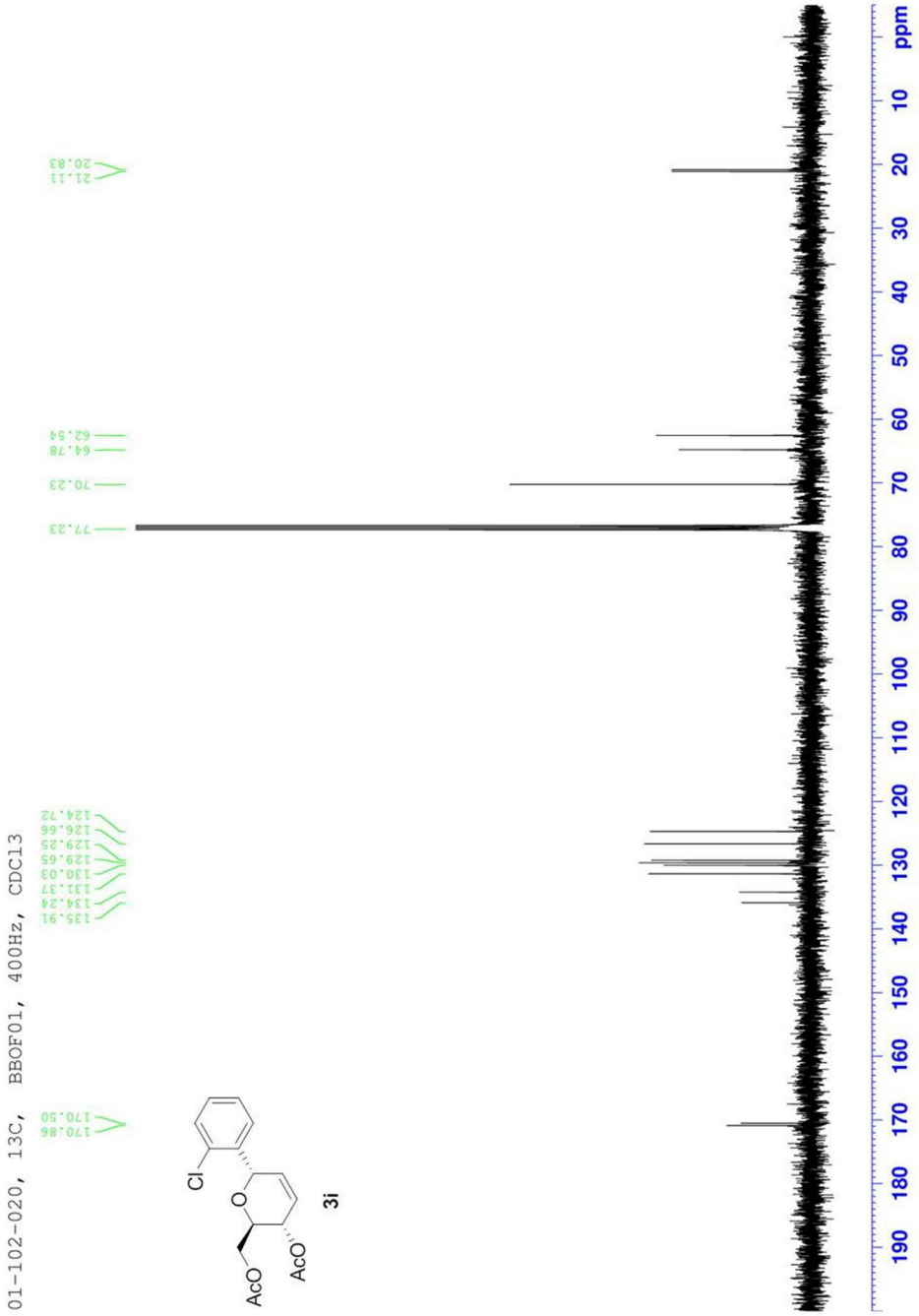

01-102-018, 1H, BBOF01, 400Hz, CDCl3
7.2856
7.2668
7.2602
7.2482
7.2236
7.2082
7.1891
7.1524
7.1339
6.2010
6.1974
6.1936
6.1903
6.1715
6.1677
6.1651
5.9967
5.9920
5.9874
5.9710
5.9661
5.9605
5.3216
5.3162
5.3123
5.3097
5.3058
5.3035
5.2971
5.2943
5.2869
4.2935
4.2787
4.2635
4.2487
4.1209
4.1132
4.0909
4.0832
3.8776
3.8698
3.8624
3.8606
3.8547
3.8532
3.8456
3.8379
2.3715
2.0906
2.0803
AcO
AcO
O
3g
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
4.26
1.00
1.00
1.00
1.96
1.03
1.01
1.00
3.00
5.97

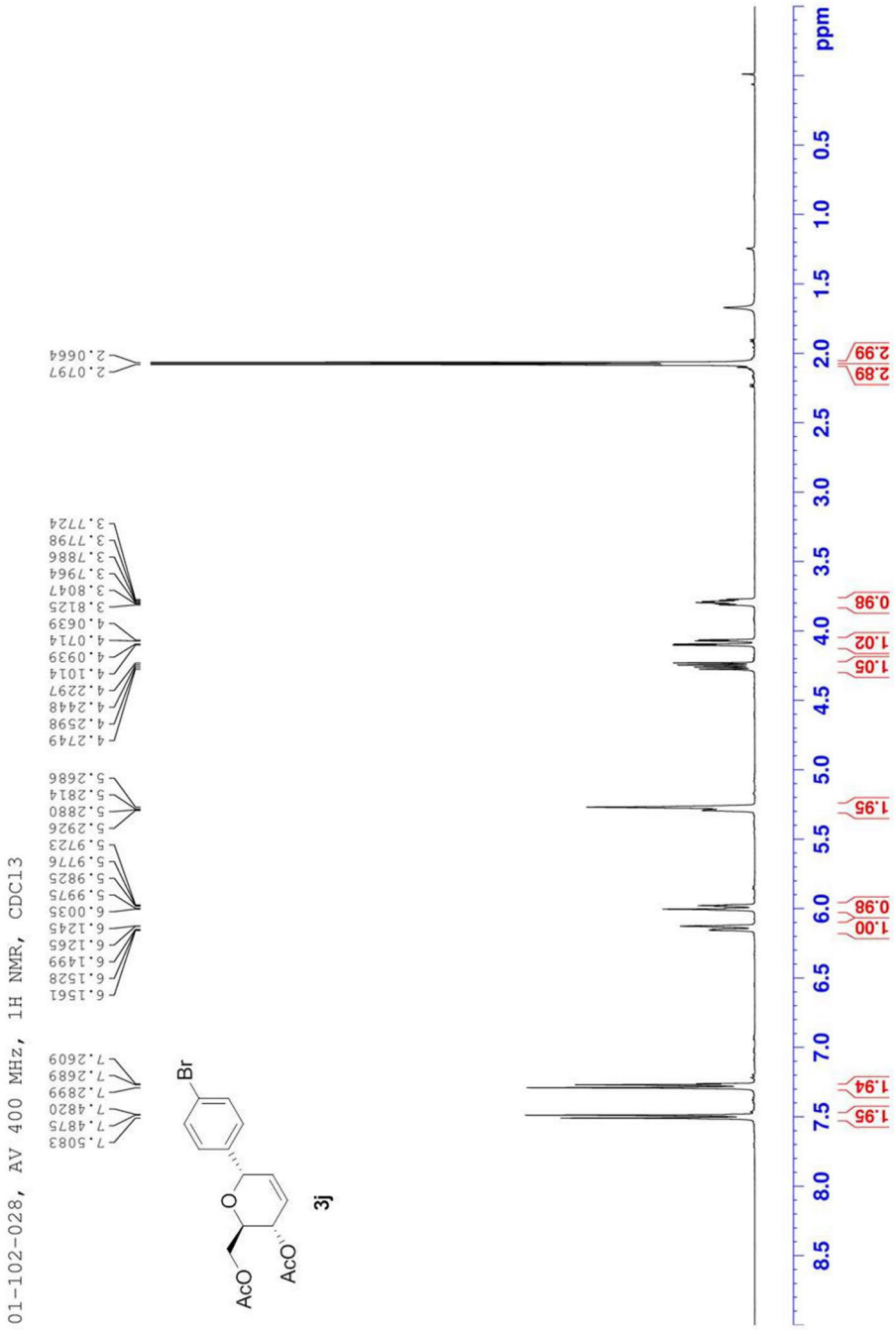

01-102-018, 13C, BBOF01, 400Hz, CDCl3
170.88
170.52
138.75
138.23
131.63
128.97
128.59
128.40
124.92
124.85
73.73
69.31
65.05
62.91
21.48
21.10
20.84
AcO
AcO
O
3g
ppm

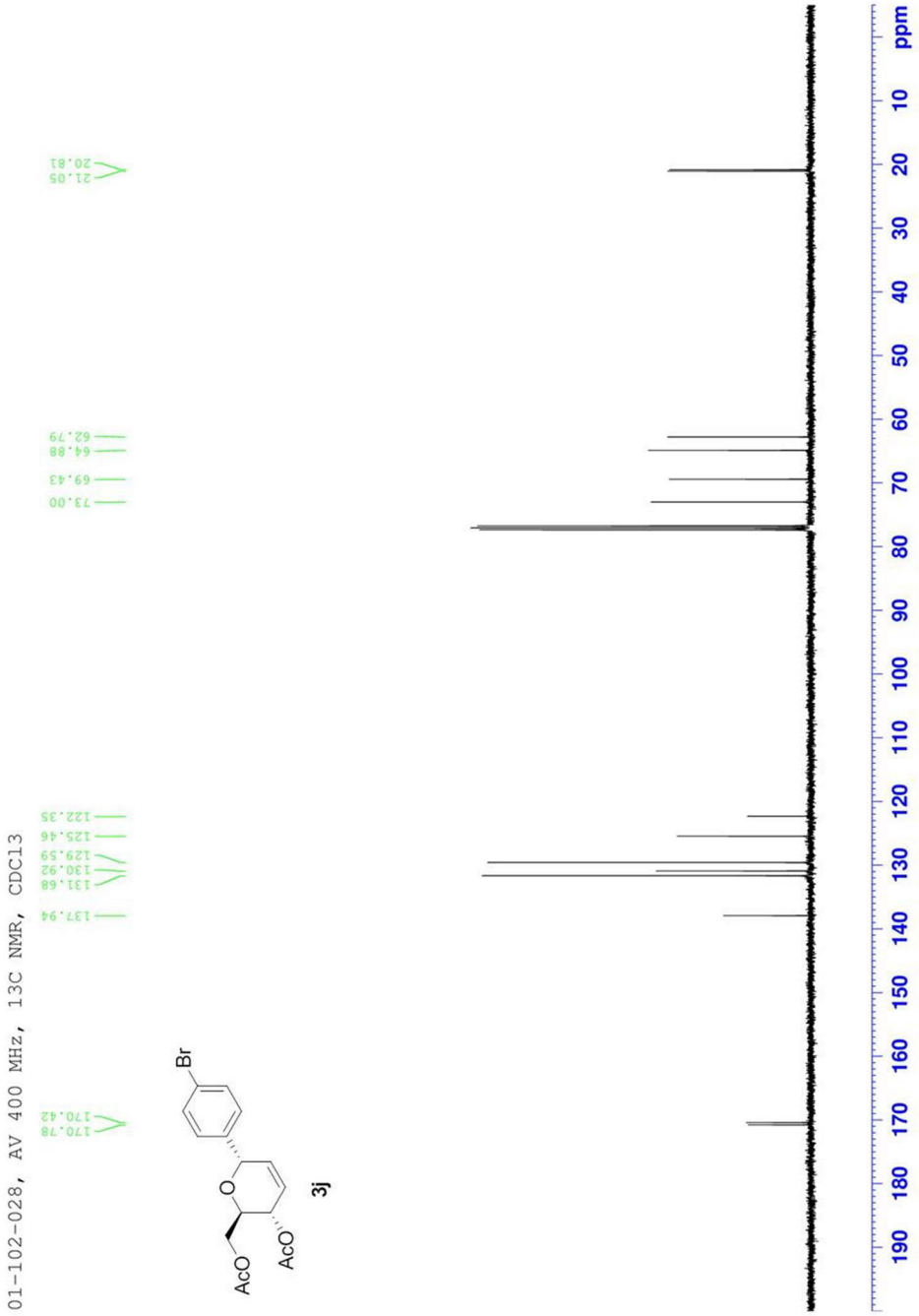

01-102-022, 1H, BBFO1 CDCl3
7.3068
7.2867
7.2600
7.1946
7.1749
6.1863
6.1828
6.1791
6.1757
6.1607
6.1569
6.1532
6.1497
5.9921
5.9870
5.9816
5.9664
5.9612
5.9560
5.3312
5.3258
5.3216
5.3156
5.3126
5.3039
5.3017
4.2816
4.2674
4.2516
4.2374
4.0930
4.0853
4.0630
4.0553
3.8440
3.8363
3.8297
3.8263
3.8222
3.8187
3.8121
3.8044
2.3583
2.0842
2.0731
AcO
AcO
O
3h
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.03
1.99
0.97
1.00
1.96
1.05
1.00
0.99
3.05
3.12
2.97

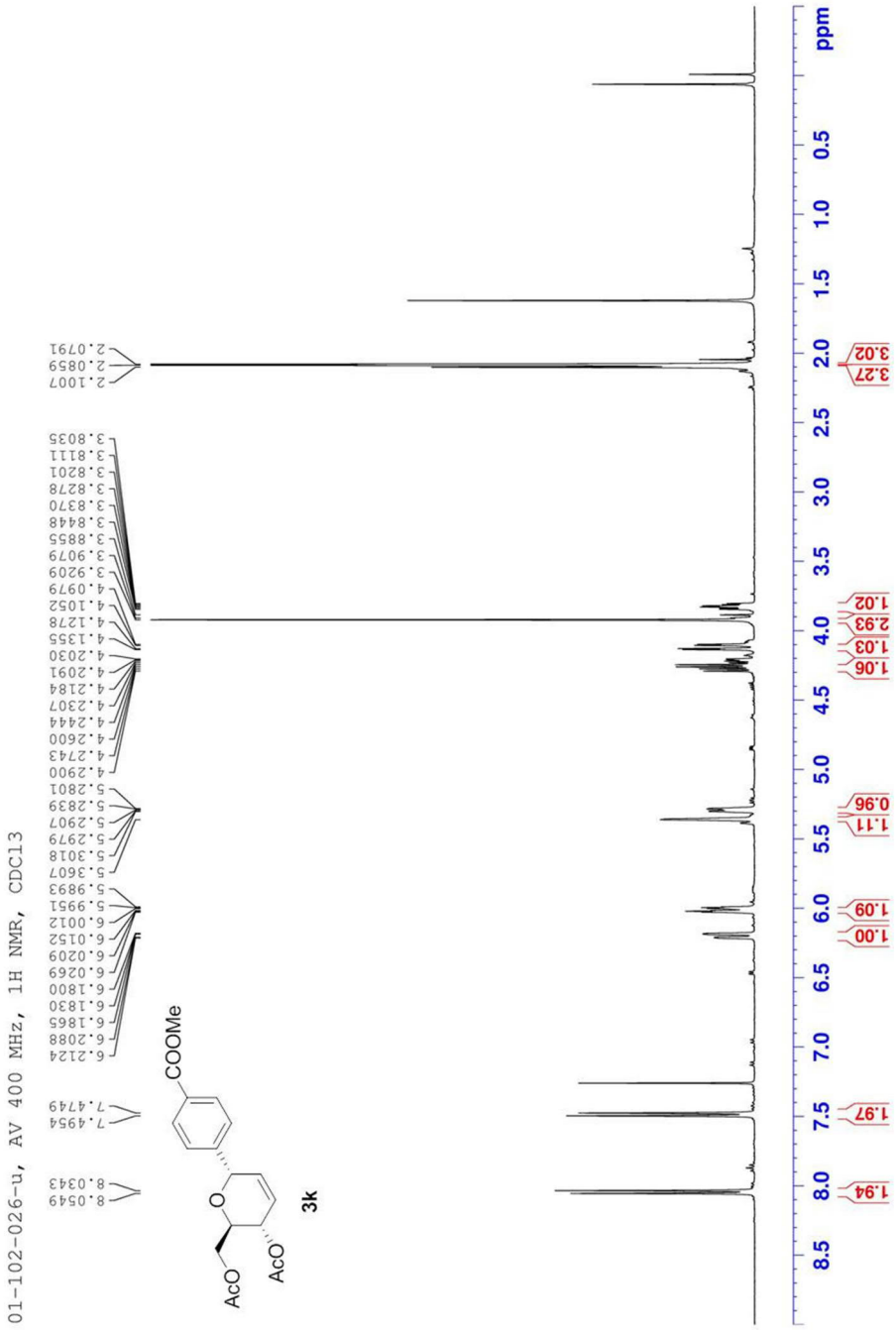

01-102-022, 13C, BBFO1 CDCl3
170.90
170.52
138.07
135.75
131.58
129.19
127.97
124.98
73.67
68.98
65.08
62.93
21.17
21.10
20.84
AcO
AcO
O
3h
ppm

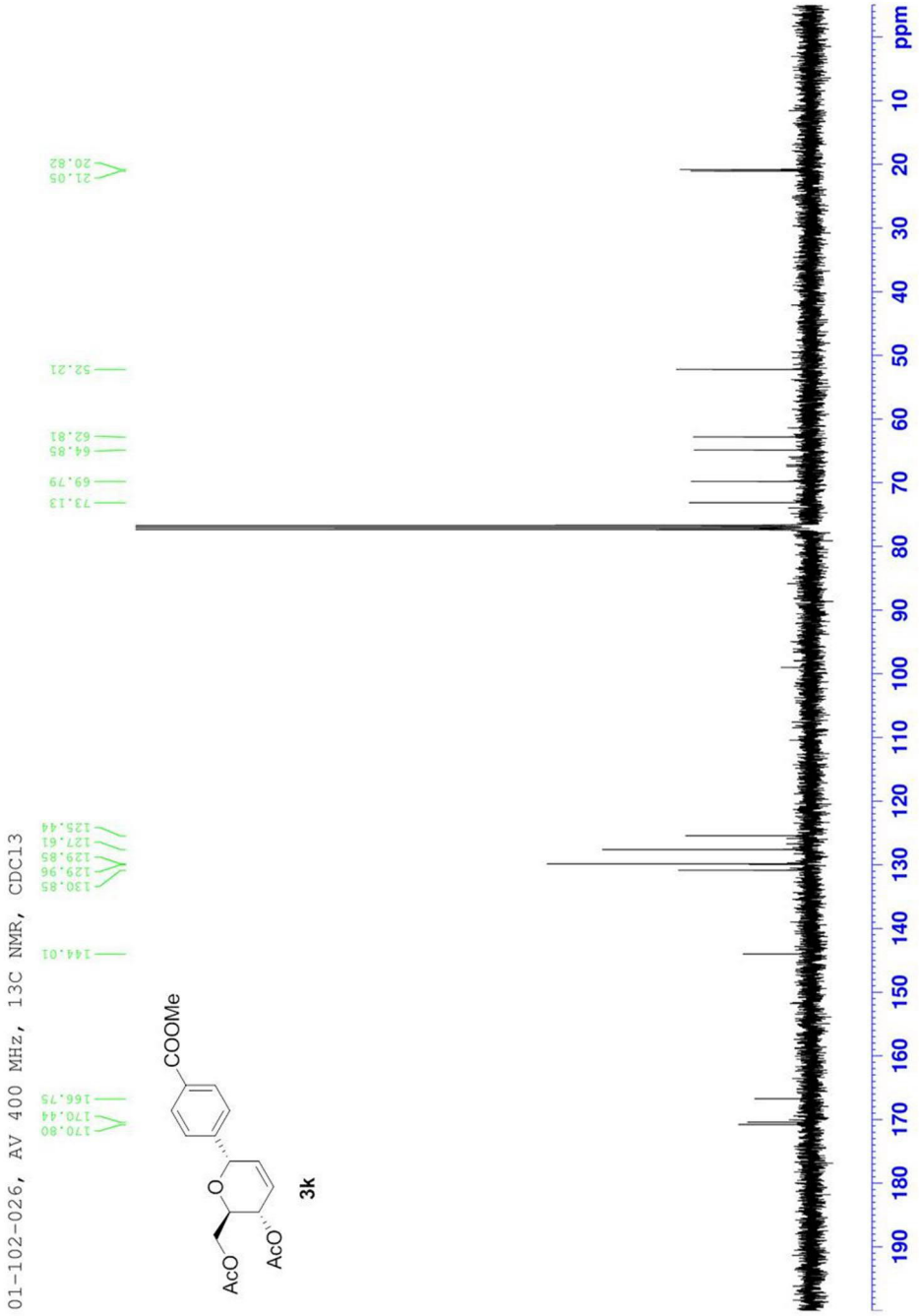

01-102-025, 1H, BBFO1 CDCl3
7.7225
7.7180
7.7061
7.7015
7.1663
7.1459
6.1595
6.1557
6.1520
6.1483
6.1332
6.1299
6.1261
6.1229
6.0127
6.0079
6.0072
6.0023
5.9874
5.9815
5.9760
5.3044
5.2989
5.2949
5.2885
5.2807
5.2771
5.2711
5.2645
5.2591
4.2801
4.2651
4.2500
4.2351
4.1043
4.0966
4.0742
4.0665
3.8145
3.8068
3.7993
3.7970
3.7918
3.7893
3.7818
3.7741
2.0860
2.0780
Cl
O
AcO
AcO
3i
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
1.90
1.90
1.90
1.03
1.03
1.99
1.09
1.07
1.00
2.84
3.01

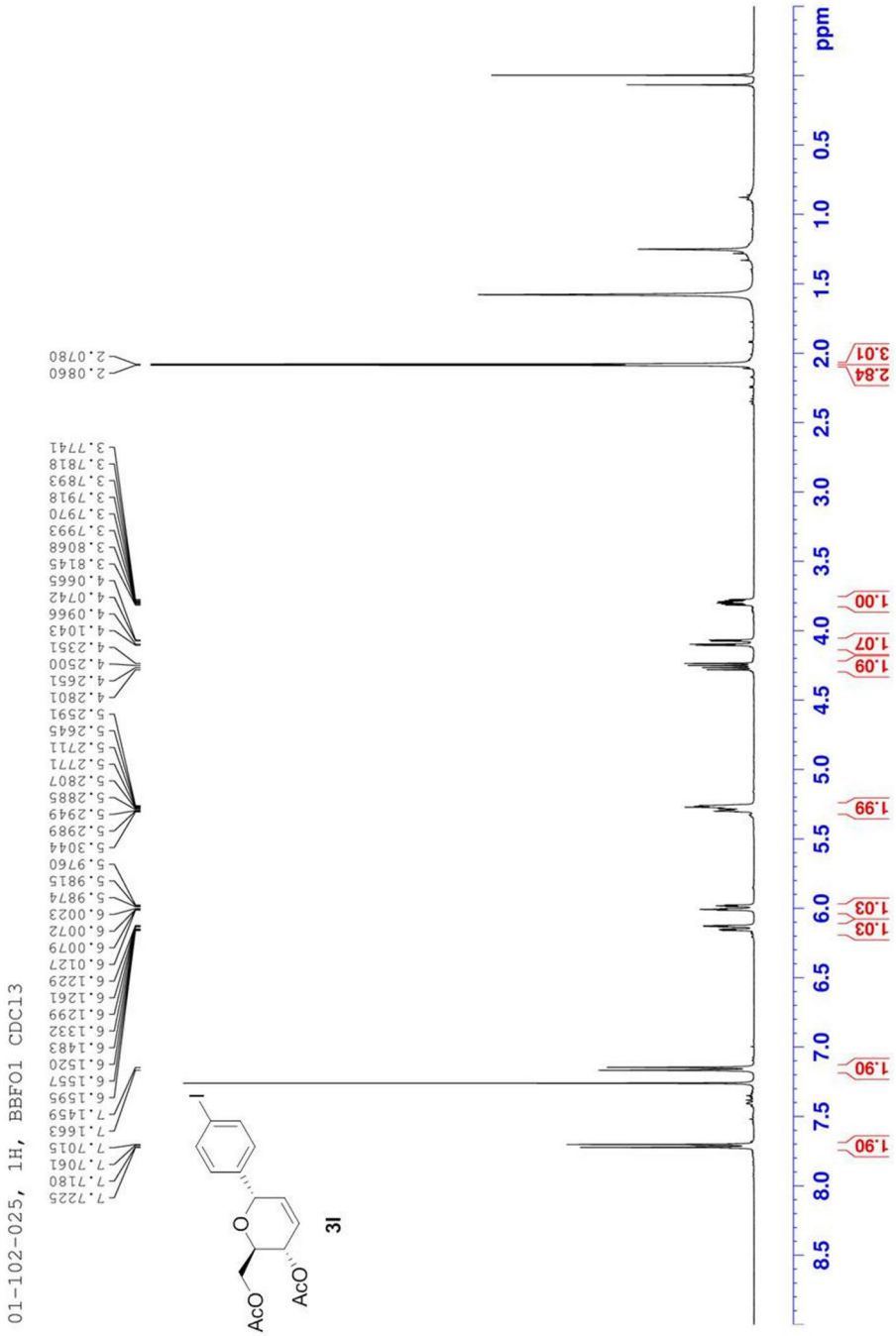

01-102-020, 13C, BBOF01, 400Hz, CDCl3
170.86
170.50
135.91
134.24
131.37
130.03
129.65
129.25
126.66
124.72
77.23
70.23
64.78
62.54
21.11
20.83
Cl
O
AcO
AcO
3i
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

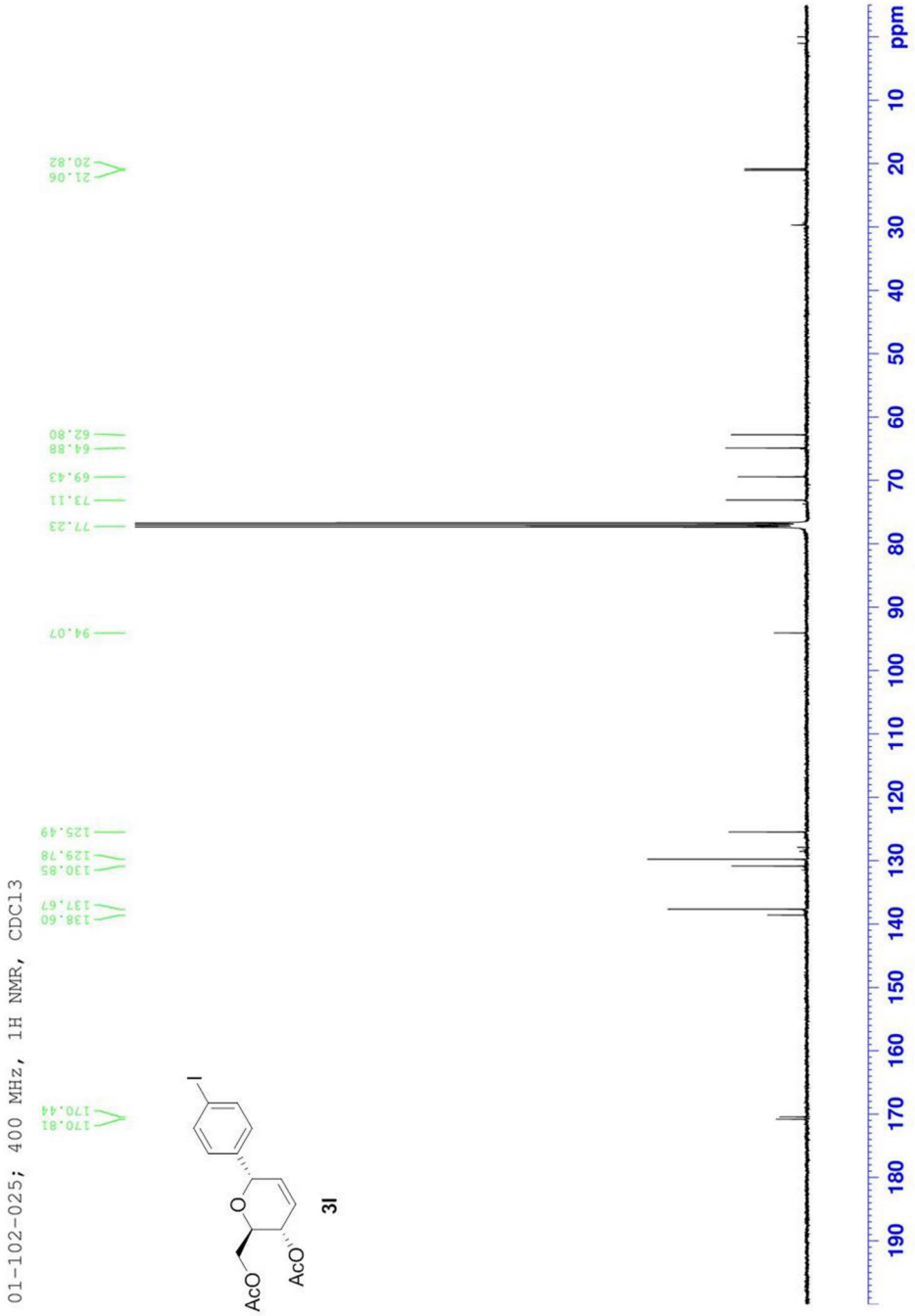

01-102-028, AV 400 MHz, 1H NMR, CDCl3
7.5083
7.4875
7.4820
7.2899
7.2689
7.2609
6.1561
6.1528
6.1499
6.1265
6.1245
6.0035
5.9975
5.9825
5.9776
5.9723
5.2926
5.2880
5.2814
5.2686
4.2749
4.2598
4.2448
4.2297
4.1014
4.0939
4.0714
4.0639
3.8125
3.8047
3.7964
3.7886
3.7798
3.7724
2.0797
2.0664
Br
O
AcO
AcO
3j
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.95
1.94
0.98
1.00
1.95
1.05
1.02
0.98
2.89
2.99

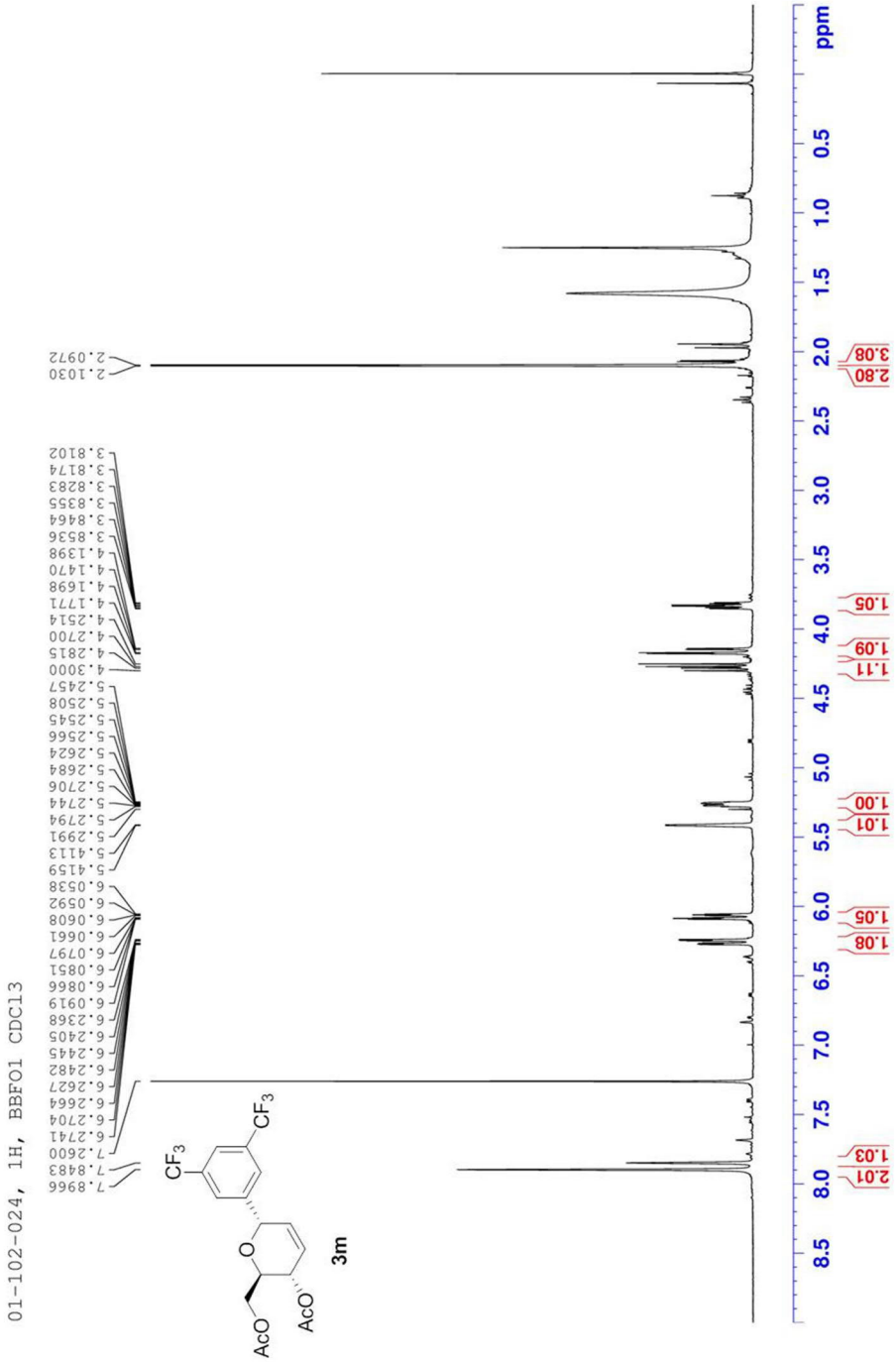

01-102-028, AV 400 MHz, 13C NMR, CDCl3
170.78
170.42
137.94
131.68
130.92
129.59
125.46
122.35
73.00
69.43
64.88
62.79
21.05
20.81
Br
O
AcO
AcO
3j
ppm

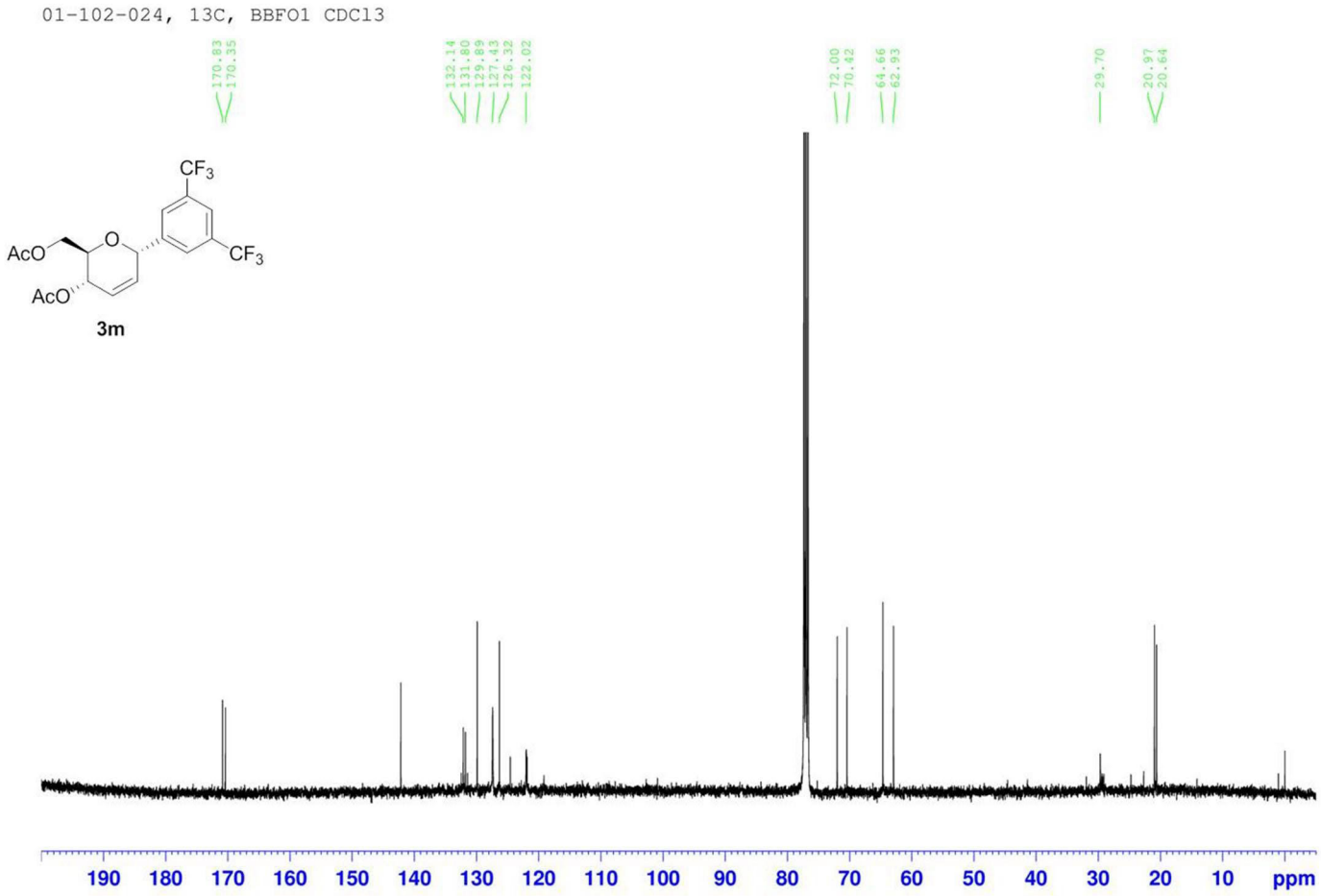

01-102-026-u, AV 400 MHz, 1H NMR, CDCl3
8.0549
8.0343
7.4954
7.4749
6.2124
6.2088
6.1865
6.1830
6.1800
6.0269
6.0209
6.0152
6.0012
5.9951
5.9893
5.3607
5.3018
5.2979
5.2907
5.2839
5.2801
4.2900
4.2743
4.2600
4.2444
4.2307
4.2184
4.2091
4.2030
4.1355
4.1278
4.1052
4.0979
3.9209
3.9079
3.8855
3.8448
3.8370
3.8278
3.8201
3.8111
3.8035
2.1007
2.0859
2.0791
COOMe
AcO
AcO
O
3k
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
1.97
1.00
1.09
1.11
0.96
1.06
1.03
2.93
1.02
3.27
3.02

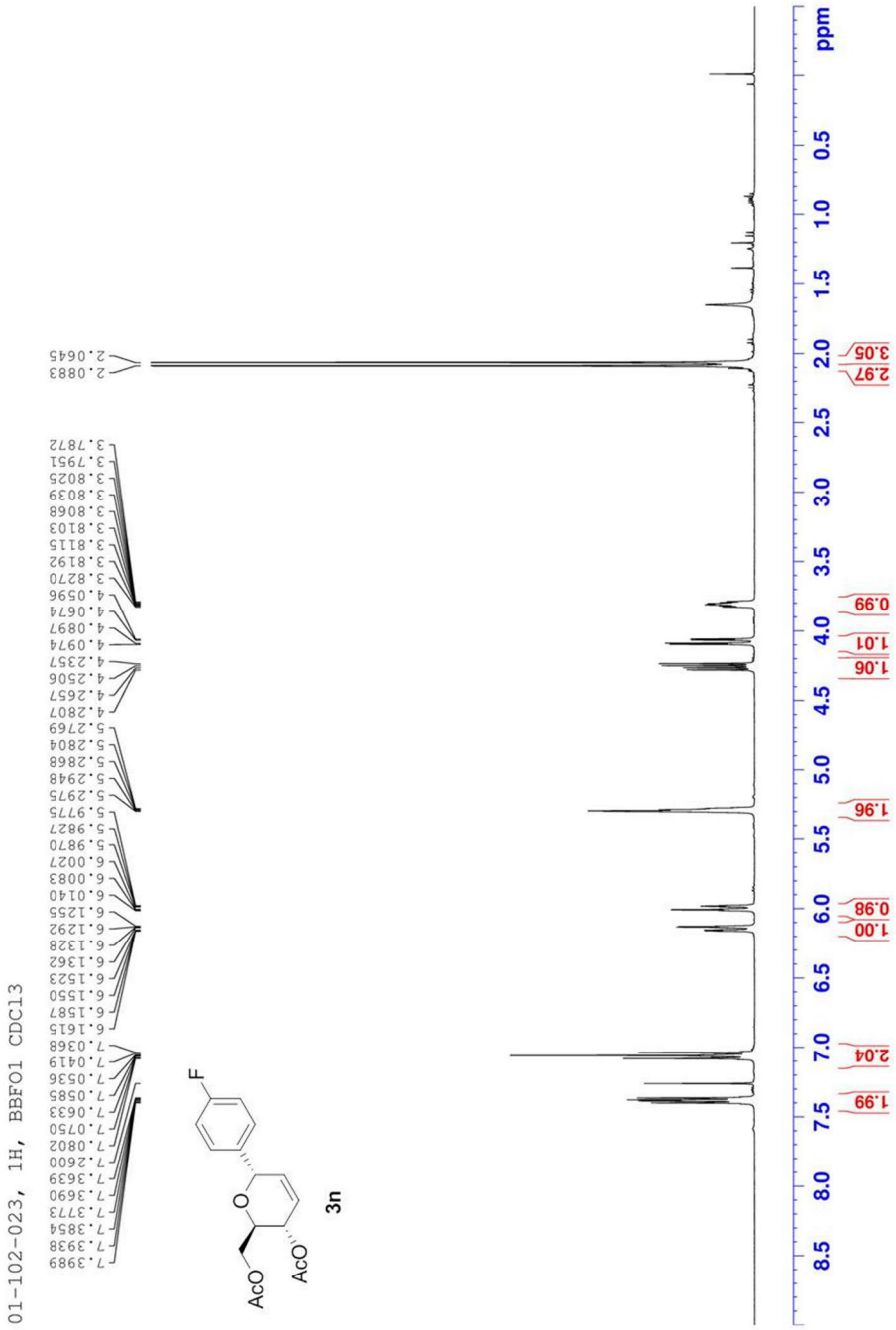

01-102-026, AV 400 MHz, 13C NMR, CDCl3
170.80
170.44
166.75
144.01
130.85
129.96
129.85
127.61
125.44
73.13
69.79
64.85
62.81
52.21
21.05
20.82
COOMe
O
AcO
AcO
3k
ppm

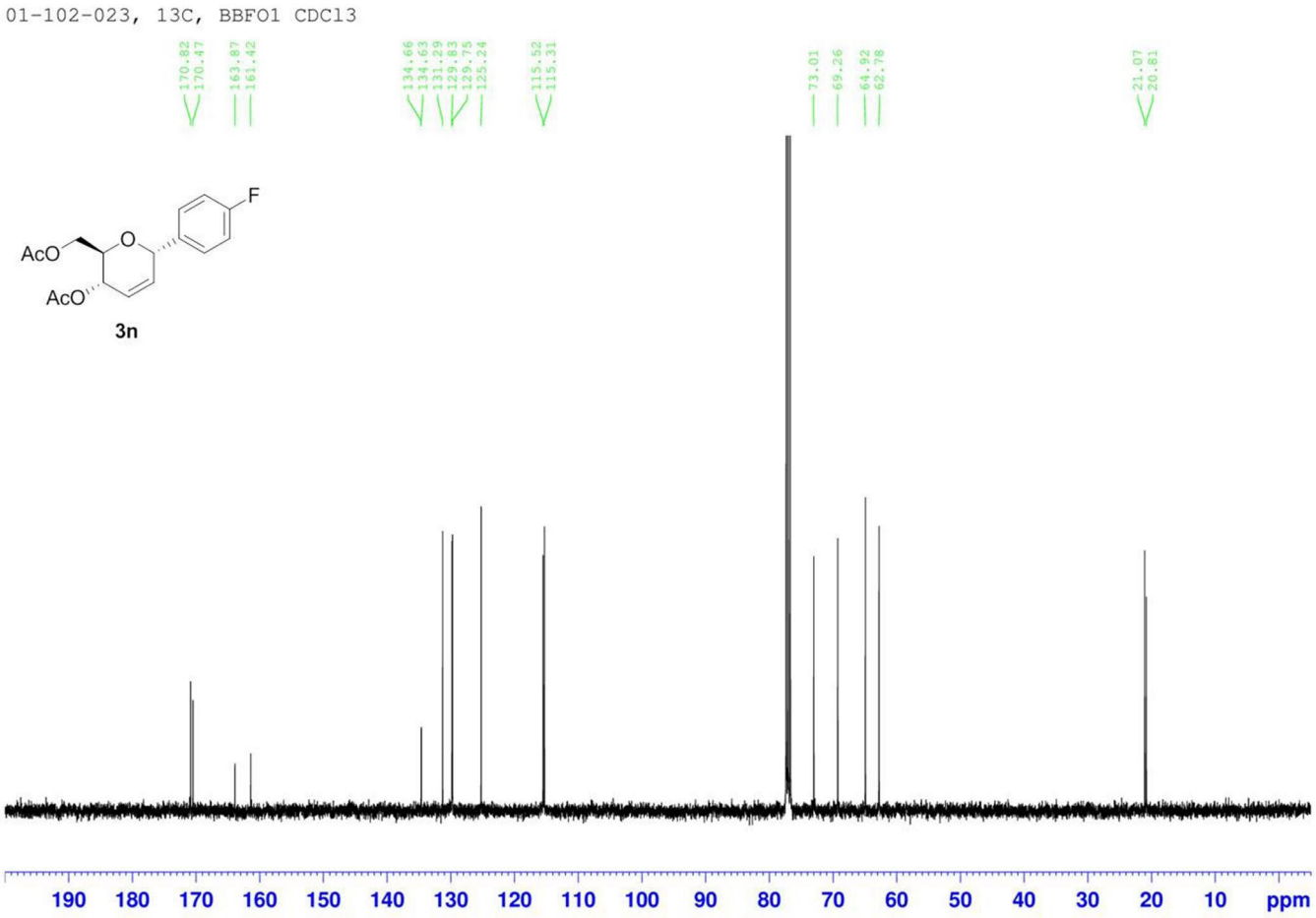

01-102-025, 1H, BBFO1 CDCl3
7.7225
7.7180
7.7061
7.7015
7.1663
7.1459
6.1595
6.1557
6.1520
6.1483
6.1332
6.1299
6.1261
6.1229
6.0127
6.0079
6.0072
6.0023
5.9874
5.9815
5.9760
5.3044
5.2989
5.2949
5.2885
5.2807
5.2771
5.2711
5.2645
5.2591
4.2801
4.2651
4.2500
4.2351
4.1043
4.0966
4.0742
4.0665
3.8145
3.8068
3.7993
3.7970
3.7918
3.7893
3.7818
3.7741
2.0860
2.0780
I
AcO
AcO
O
3l
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
1.90
1.90
1.90
1.03
1.03
1.99
1.09
1.07
1.00
2.84
3.01

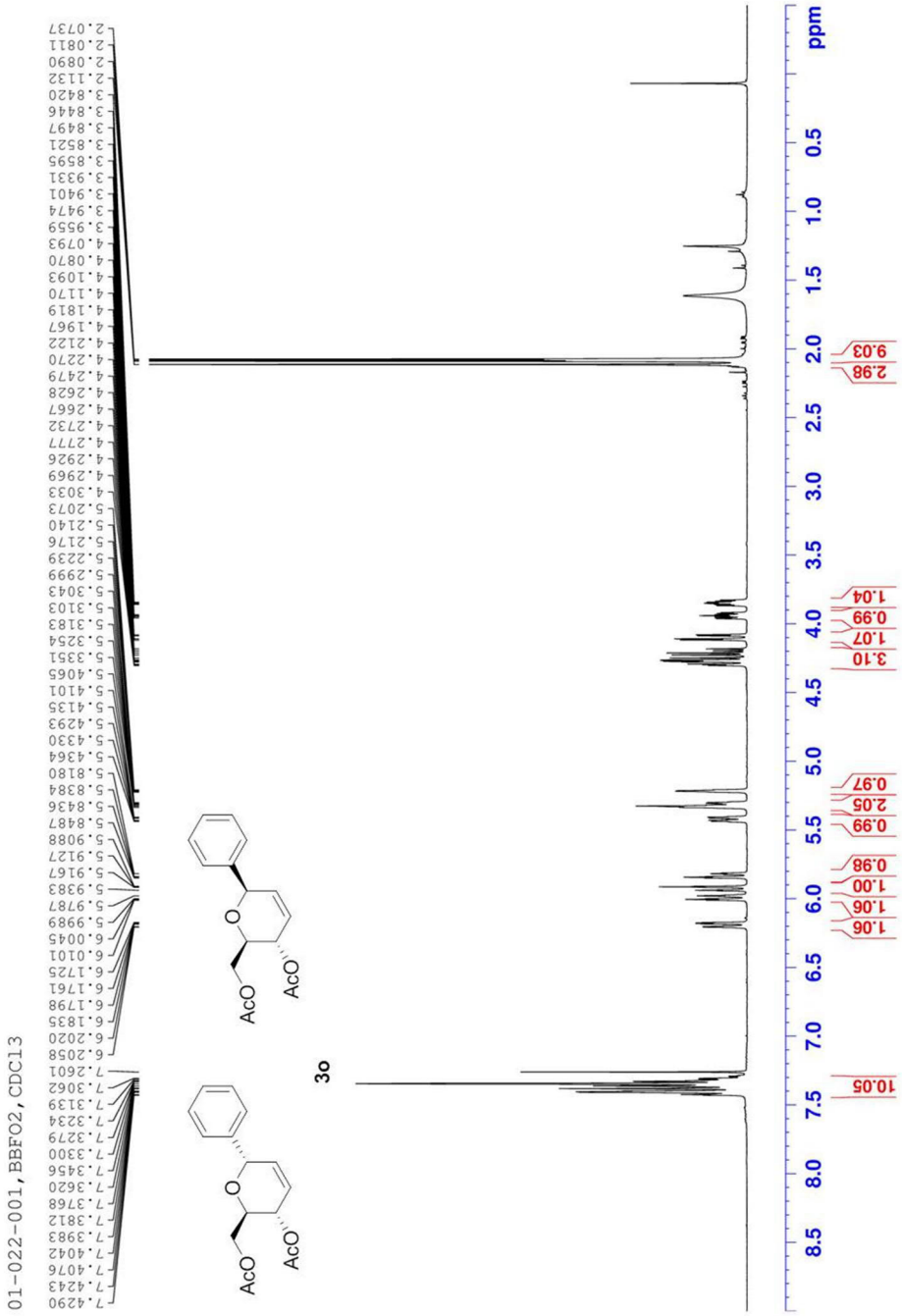

01-102-025; 400 MHz, 1H NMR, CDCl3
170.81
170.44
138.60
137.67
130.85
129.78
125.49
94.07
77.23
73.11
69.43
64.88
62.80
21.06
20.82
AcO
AcO
O
I
3l
ppm

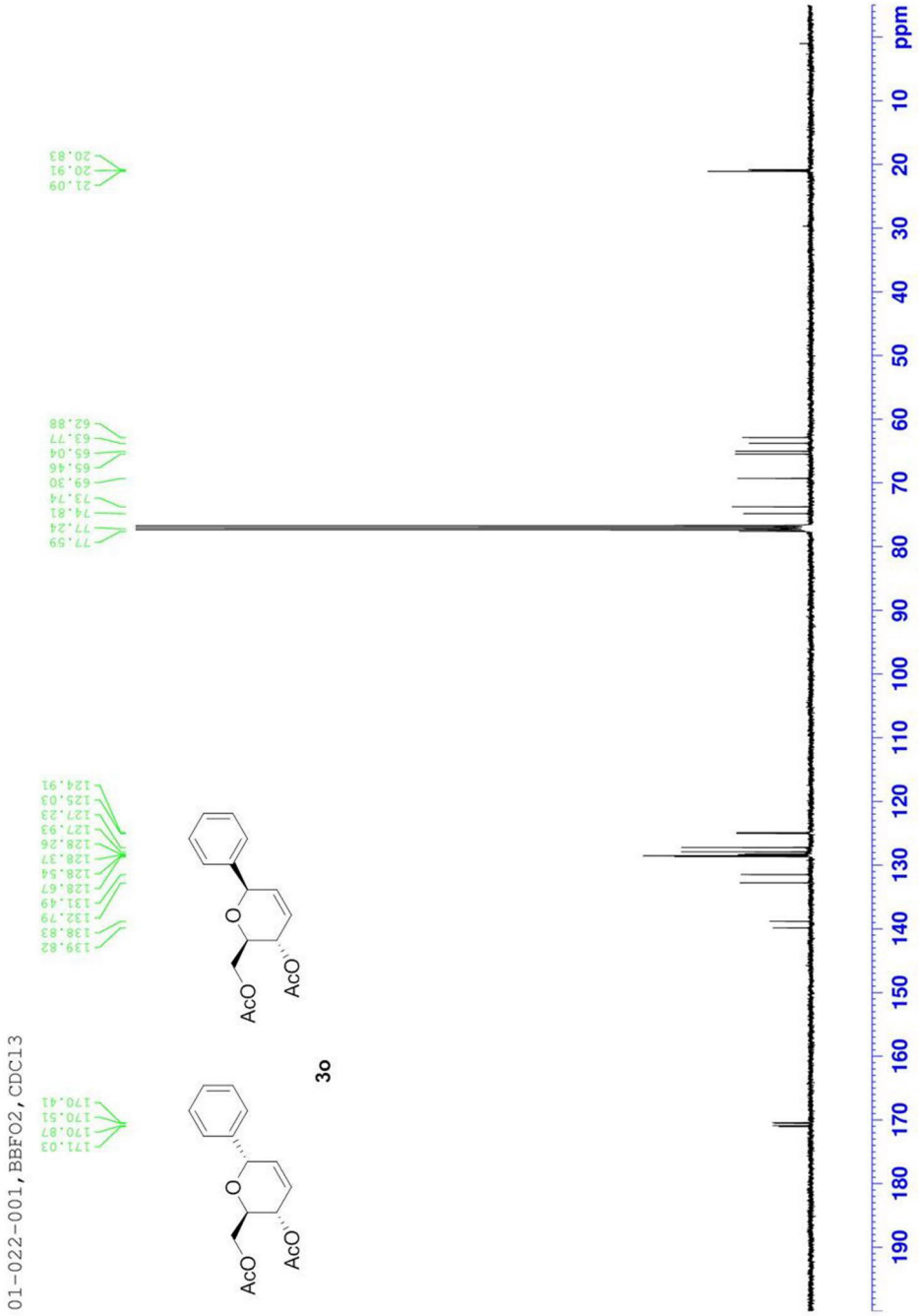

01-102-024, 1H, BBFO1 CDCl3
7.8966
7.8483
7.2600
6.2741
6.2704
6.2664
6.2627
6.2482
6.2445
6.2405
6.2368
6.0919
6.0866
6.0851
6.0797
6.0661
6.0608
6.0592
6.0538
5.4159
5.4113
5.2991
5.2794
5.2744
5.2706
5.2684
5.2624
5.2566
5.2545
5.2508
5.2457
4.3000
4.2815
4.2700
4.2514
4.1771
4.1698
4.1470
4.1398
3.8536
3.8464
3.8355
3.8283
3.8174
3.8102
2.1030
2.0972
CF3
CF3
O
AcO
AcO
3m
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.01
1.03
1.05
1.08
1.01
1.00
1.11
1.09
1.05
2.80
3.08

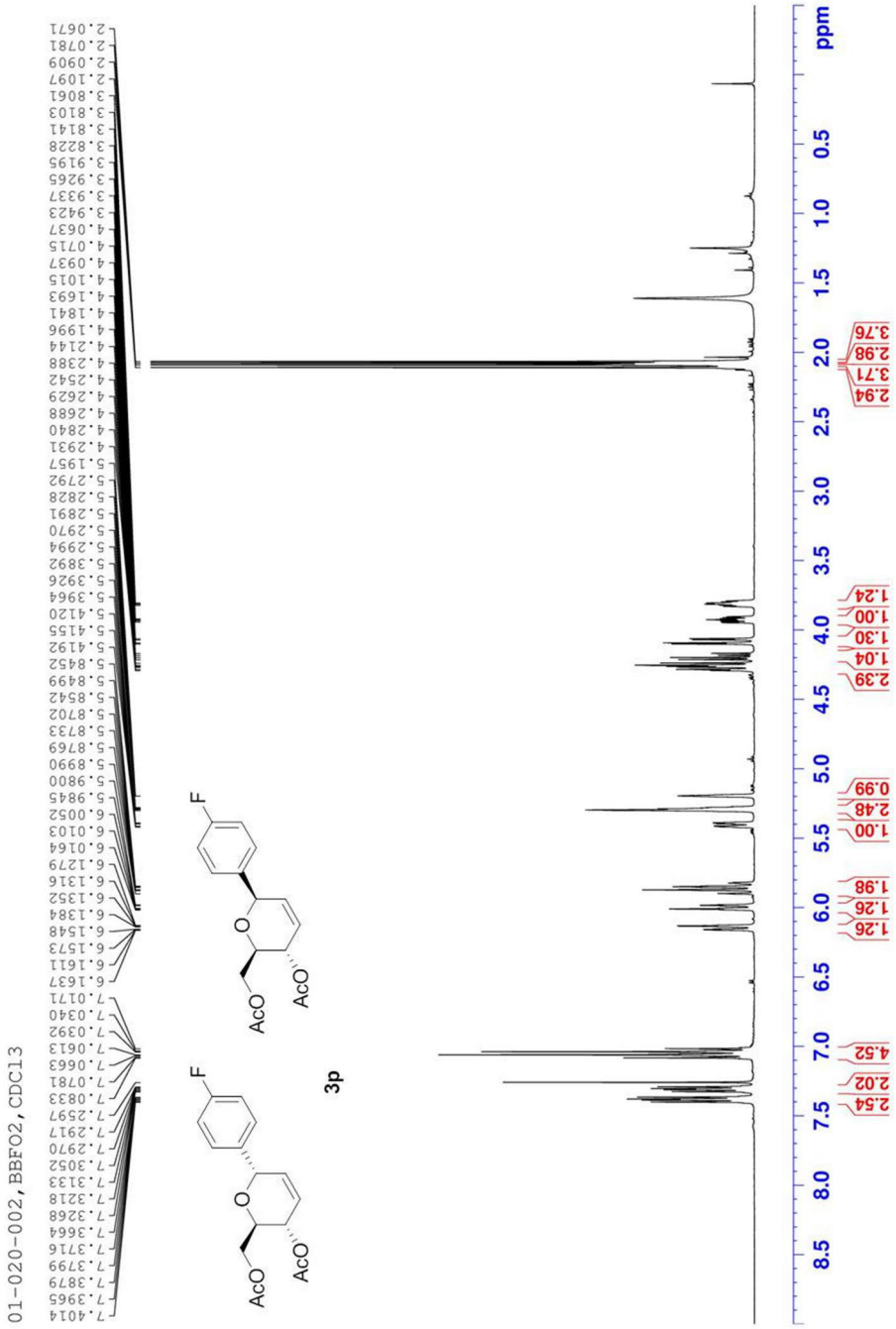

01-102-024, 13C, BBFO1 CDCl3
170.83
170.35
132.14
131.80
129.89
127.43
126.32
122.02
72.00
70.42
64.66
62.93
29.70
20.97
20.64
CF3
CF3
AcO
AcO
O
3m
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

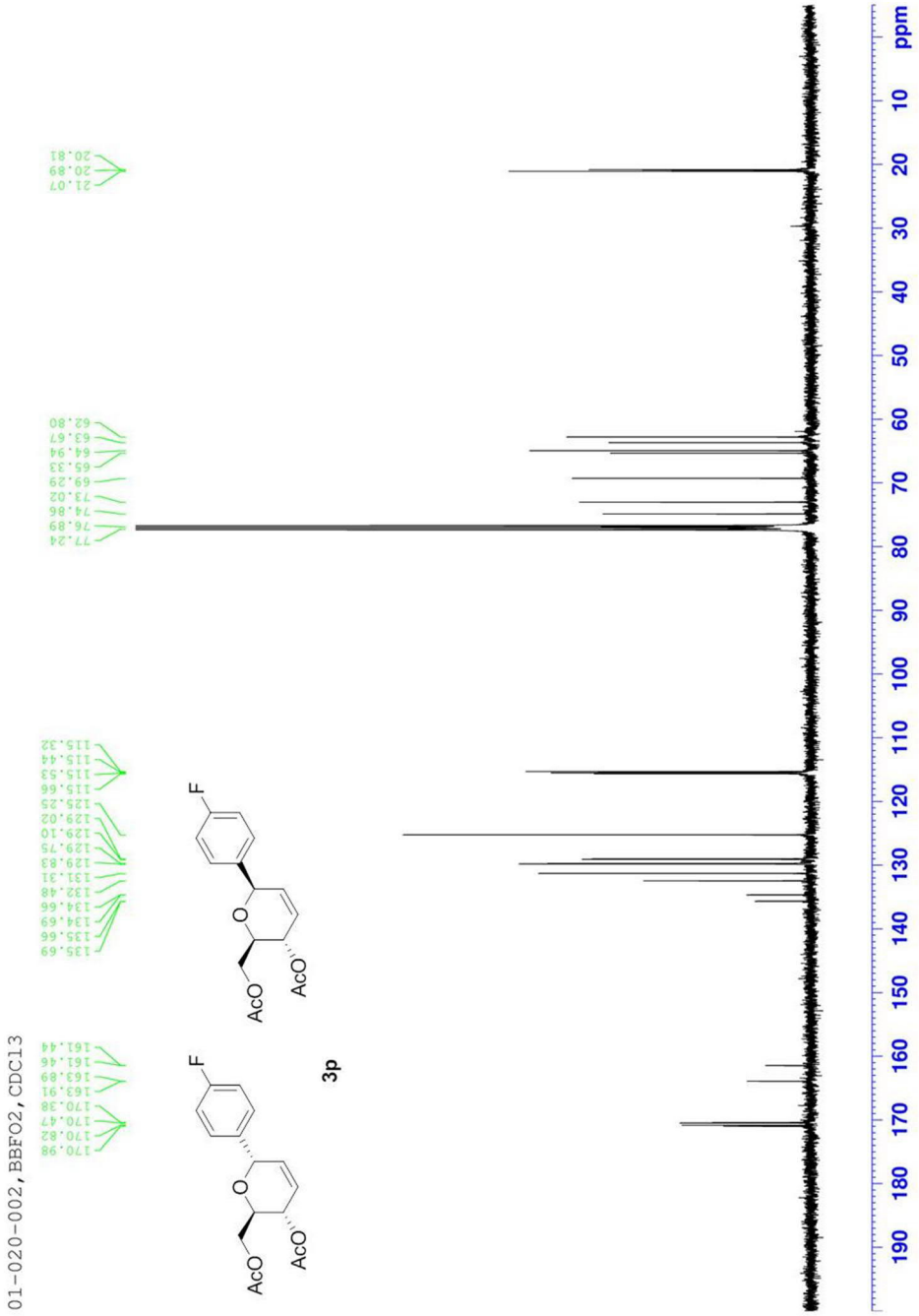

01-102-023, 1H, BBFO1 CDCl3
7.3989
7.3938
7.3854
7.3773
7.3690
7.3639
7.2600
7.0802
7.0750
7.0633
7.0585
7.0536
7.0419
7.0368
6.1615
6.1587
6.1550
6.1523
6.1362
6.1328
6.1292
6.1255
6.0140
6.0083
6.0027
5.9870
5.9827
5.9775
5.2975
5.2948
5.2868
5.2804
5.2769
4.2807
4.2657
4.2506
4.2357
4.0974
4.0897
4.0674
4.0596
3.8270
3.8192
3.8115
3.8103
3.8068
3.8039
3.8025
3.7951
3.7872
2.0883
2.0645
F
O
AcO
AcO
3n
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.99
2.04
0.98
1.00
1.96
1.06
1.01
0.99
2.97
3.05

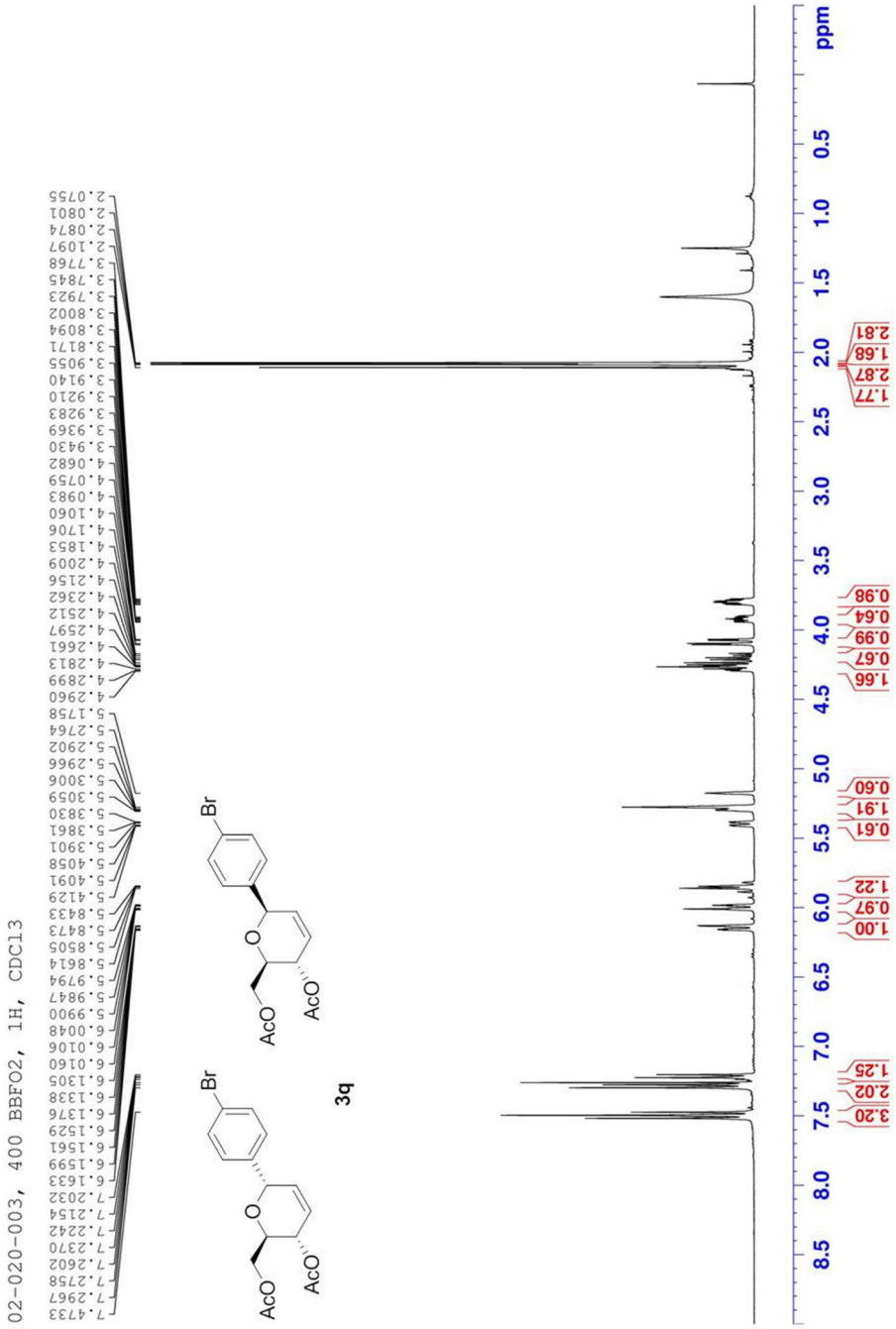

01-102-023, 13C, BBFO1 CDCl3
170.82
170.47
163.87
161.42
134.66
134.63
131.29
129.83
129.75
125.24
115.52
115.31
73.01
69.26
64.92
62.78
21.07
20.81
AcO
AcO
O
F
3n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

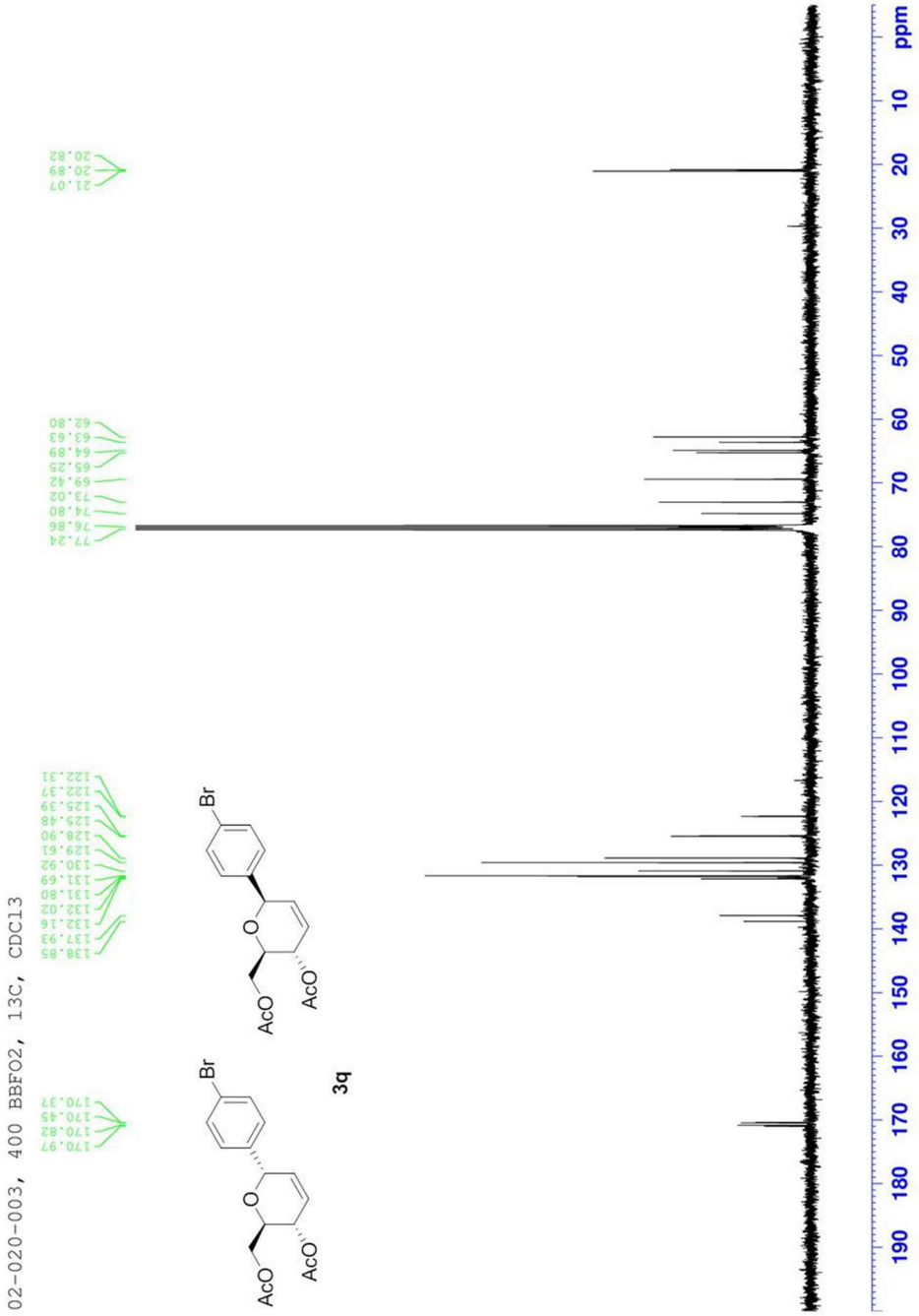

01-022-001,BBFO2,CDCl3
7.4290
7.4243
7.4076
7.4042
7.3983
7.3812
7.3768
7.3620
7.3456
7.3300
7.3279
7.3234
7.3139
7.3062
7.2601
6.2058
6.2020
6.1835
6.1798
6.1761
6.1725
6.0101
6.0045
5.9989
5.9787
5.9383
5.9167
5.9127
5.9088
5.8487
5.8436
5.8384
5.8180
5.4364
5.4330
5.4293
5.4135
5.4101
5.4065
5.3351
5.3254
5.3183
5.3103
5.3043
5.2999
5.2239
5.2176
5.2140
5.2073
4.3033
4.2926
4.2969
4.2777
4.2732
4.2667
4.2628
4.2479
4.2270
4.2122
4.1967
4.1819
4.1170
4.1093
4.0870
4.0793
3.9559
3.9474
3.9401
3.9331
3.8595
3.8521
3.8497
3.8446
3.8420
2.1132
2.0890
2.0811
2.0737
AcO
AcO
O
AcO
AcO
O
3o
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
10.05
1.06
1.06
1.00
0.98
0.99
2.05
0.97
3.10
1.07
0.99
1.04
2.98
9.03

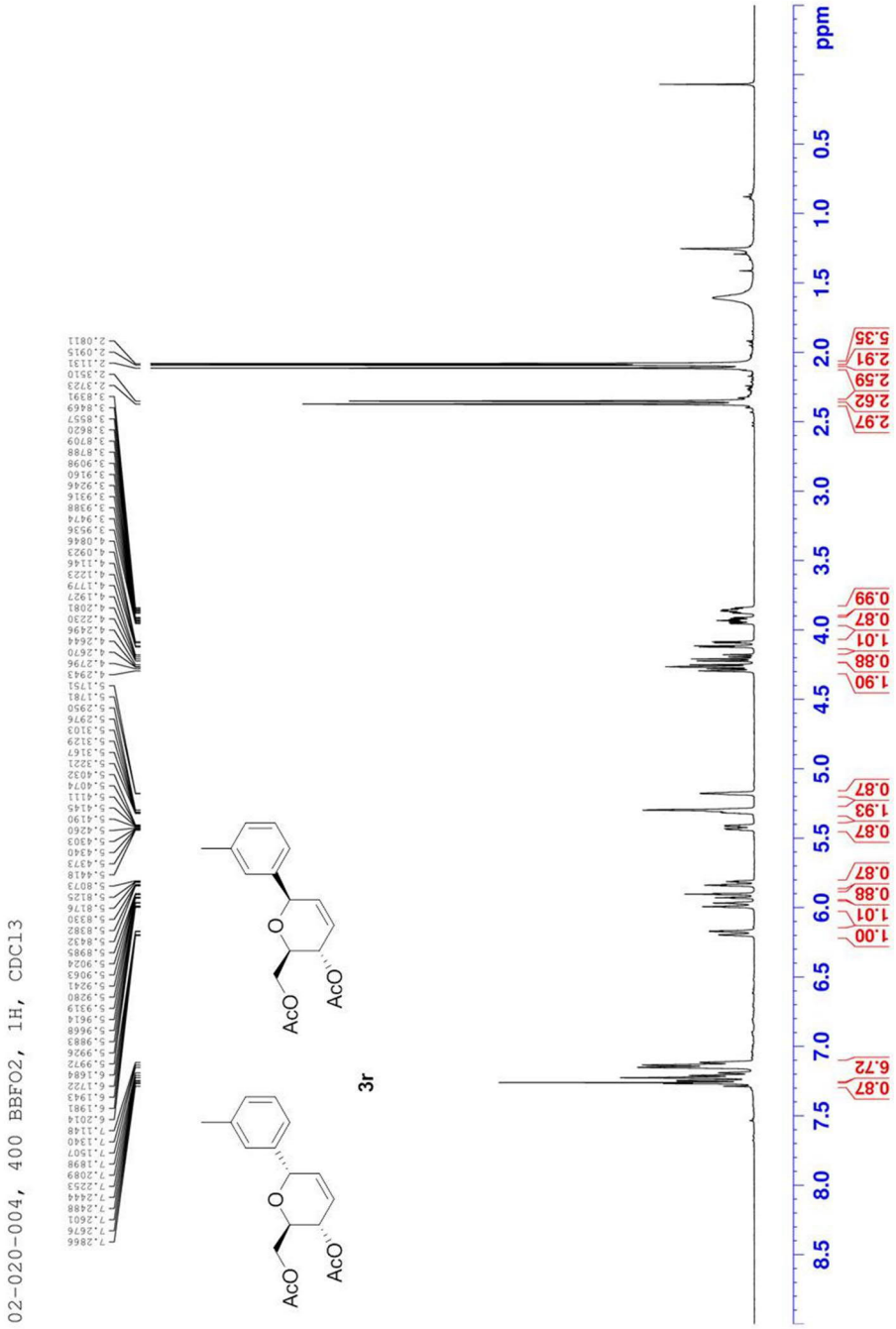

01-022-001,BBFO2,CDC13
171.03
170.87
170.51
170.41
139.82
138.83
132.79
131.49
128.67
128.54
128.37
128.26
127.93
127.23
125.03
124.91
77.59
77.24
74.81
73.74
69.30
65.46
65.04
63.77
62.88
21.09
20.91
20.83
AcO
AcO
O
AcO
AcO
O
3o
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

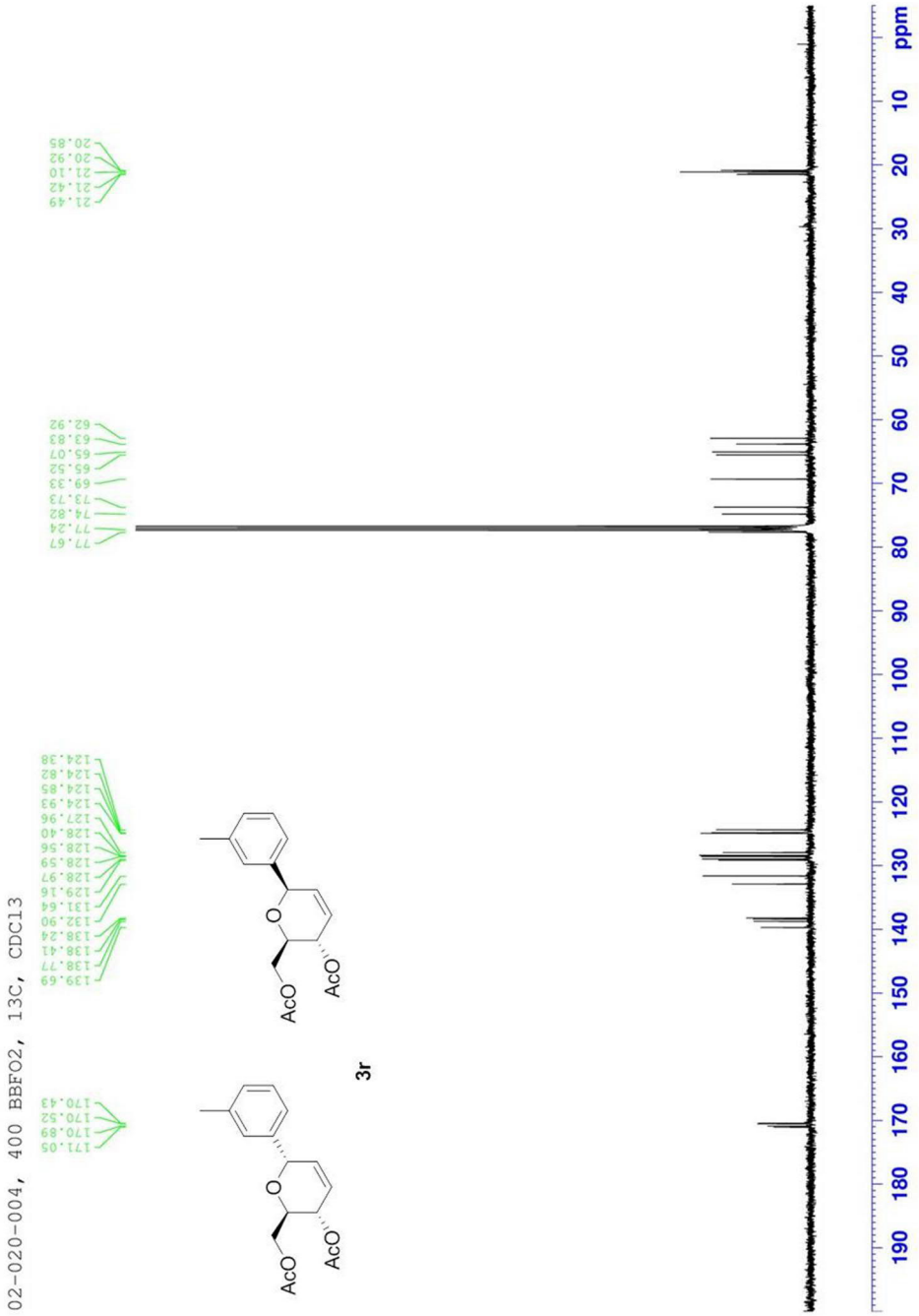

01-020-002,BBFO2,CDCl3
3p
AcO
AcO
O
F
ppm

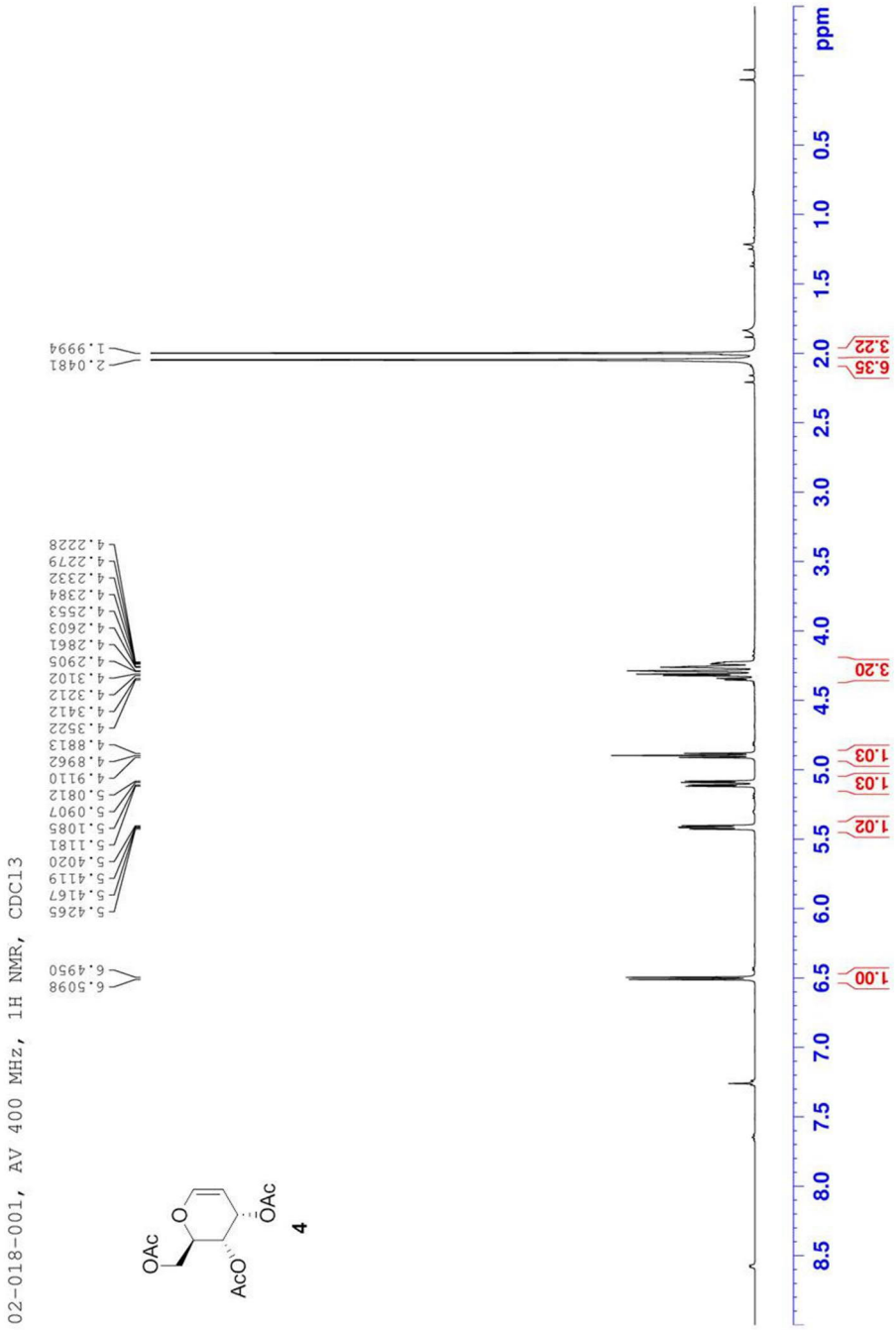

01-020-002,BBFO2,CDCl3
170.98
170.82
170.47
170.38
163.91
163.89
161.46
161.44
135.69
135.66
134.69
134.66
132.48
131.31
129.83
129.75
129.10
129.02
125.25
115.66
115.53
115.44
115.32
77.24
76.89
74.86
73.02
69.29
65.33
64.94
63.67
62.80
21.07
20.89
20.81
F
AcO
AcO
O
3p
ppm


02-020-003, 400 BBFO2, 1H, CDCl3
7.4733
7.2967
7.2758
7.2602
7.2370
7.2242
7.2154
7.0032
6.1633
6.1599
6.1561
6.1529
6.1376
6.1338
6.1305
6.0160
6.0106
6.0048
5.9900
5.9847
5.9794
5.8614
5.8505
5.8473
5.8433
5.4129
5.4091
5.4058
5.3901
5.3861
5.3830
5.3059
5.3006
5.2966
5.2902
5.2764
5.1758
4.2960
4.2899
4.2813
4.2661
4.2597
4.2512
4.2362
4.2156
4.2009
4.1853
4.1706
4.1060
4.0983
4.0759
4.0682
3.9430
3.9369
3.9283
3.9210
3.9140
3.9055
3.8171
3.8094
3.8002
3.7923
3.7845
3.7768
2.1097
2.0874
2.0801
2.0755
Br
AcO
AcO
O
Br
AcO
AcO
O
3q
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
3.20
2.02
1.25
1.00
0.97
1.22
0.61
1.91
0.60
1.66
0.67
0.99
0.64
0.98
1.77
2.87
1.68
2.81


02-020-003, 400 BBFO2, 13C, CDCl3
170.97
170.82
170.45
170.37
138.85
137.93
132.16
132.02
131.80
131.69
130.92
129.61
128.90
129.48
129.39
122.37
122.31
77.24
76.86
74.80
73.02
69.42
65.25
64.89
63.63
62.80
21.07
20.89
20.82
Br
O
AcO
AcO
3q
ppm


02-020-004, 400 BBFO2, 1H, CDCl3
AcO
AcO
O
AcO
AcO
O
3r
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.87
6.72
1.00
1.01
0.88
0.87
0.87
1.93
0.87
1.90
0.88
1.01
0.87
0.99
2.97
2.62
2.59
2.91
5.35


02-020-004, 400 BBFO2, 13C, CDCl3
171.05
170.89
170.52
170.43
139.69
138.77
138.41
138.24
132.90
131.64
129.16
128.97
128.59
128.56
128.40
127.96
124.93
124.85
124.82
124.38
77.67
77.24
74.82
73.73
69.33
65.52
65.07
63.83
62.92
21.49
21.42
21.10
20.92
20.85
AcO
AcO
O
AcO
AcO
O
3r
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


02-018-001, AV 400 MHz, 1H NMR, CDCl3
OAc
AcO
OAc
O
4
6.5098
6.4950
5.4265
5.4167
5.4119
5.4020
5.1181
5.1085
5.0907
5.0812
4.9110
4.8962
4.8813
4.3522
4.3412
4.3212
4.3102
4.2905
4.2861
4.2603
4.2553
4.2384
4.2332
4.2279
4.2228
2.0481
1.9994
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
1.02
1.03
1.03
3.20
6.35
3.22

02-018-001, AV 400 MHz, 13C NMR, CDCl3